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Journal of Organometallic Chemistry 617–618 (2001) 383–394

Journal of Organo metallic Chemistry

Complexes with phosphorus analogues of imidazoyl carbenes: unprecedented formation of phosphenium complexes by coordination induced P–Cl bond heterolysis

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Received 26 July 2000; accepted 1 September 2000

Dedicated to Professor Manfred Regitz on the occasion of his 65th birthday

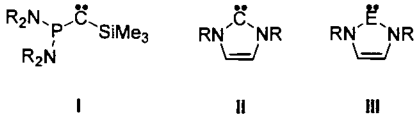
Abstract

Diazaphospholenium complexes are readily accessible from reactions of complexes [M(bipy)(CO)$_3$(L)] (L = CO, MeCN, M = Mo, W) with both the 1,3-dimesityl-4-chloro-1,3,2-diazaphospholenium triflate (**1**) [OTf] and the corresponding *p*-chloro-diazaphospholene (**8**). The latter reaction proceeds via an unprecedented coordination induced ionisation of P–Cl bonds, which requires no further assistance by an external electrophile. The complexes were found to be configurationally stable, but may undergo selective substitution of *trans*-ligands with retention of the phosphenium moiety. All compounds were characterised by analytical and spectroscopic techniques, and two of the complexes were investigated by single-crystal X-ray diffraction. The spectroscopic and structural data provide evidence for considerable M–P double bond character which, leads to a marked reduction of π-delocalization in the diazaphospholenium unit. Studies of metal NMR spectra of tungsten complexes revealed further, a linear correlation between $\delta\,^{183}$W and $^1J_{WP}$ which allows monitoring of trends in metal–phosphorus multiple bonding. Surprisingly, spectroscopic and structural data suggest that the cation **1** displays a higher π-acceptor ability than an analogous CC-saturated heterocyclic phosphenium ligand, which contrasts with the lower electrophilicity of **1** with respect to unconjugated diaminophosphenium species. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbene analogues; Phosphenium complexes; π-Acceptor ligands; Metal–ligand multiple bonding; Bond heterolysis

1. Introduction

Transition metal carbene complexes [1] are known for some 40 years, and their unique reactivity have made them indispensable reagents in organometallic chemistry, organic synthesis, and catalysis [2]. Even though various synthetic approaches to carbene complexes have been devised [2], one of the most fundamental routes, viz. direct reaction of a transition metal precursor complex with a free carbene, has long remained unexplored owing to the lack of sufficiently stable carbenes. The situation changed merely some 10 years ago when the groups of Bertrand [3] and Arduengo [4] described the first carbene derivatives of the type **I** and **II** which could be isolated as stable compounds and were accessible on a preparative scale. This discovery triggered extensive studies of the synthesis of new stable carbenes and the exploration of their electronic structures and chemical reactivities, including their potential for complex formation. The major achievements in this area during the last years have been recently comprehensively reviewed [2,5] (Scheme 1).



Scheme 1.

The renaissance of carbene chemistry has also encouraged studies of carbene analogues which are ob-

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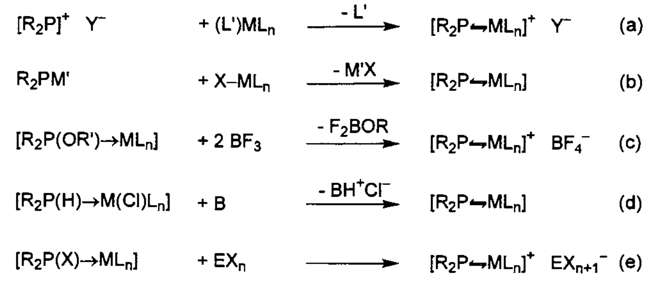
PII: S0022-328X(00)00624-0



Scheme 2. Known synthetic pathways to phosphenium complexes.

tained by formal isoelectronic replacement of the divalent carbon by another p-block element. Most of these investigations focused on the variation of the structural motif of imidazoyl carbenes, **II**, and a wealth of subvalent main group compounds **III** are now known which include both neutral compounds with heavier Group 14 elements ($E = Si$, Ge) [6] and ionic species containing a positively or negatively charged element of an adjacent main group ($E = Ga^-$, N^+, P^+) [7]. A common feature of all these derivatives which stimulated intensive research is the presence of six π-electrons in the ring which offer the possibility of aromatic stabilisation. It has, meanwhile, been established that (i) aromaticity contributes far less to the overall stability than $N \rightarrow E$ π-donation into the empty p-orbital at the divalent element [8]; and (ii) the extent of cyclic π-delocalisation in phosphenium cations (**III**, $E = P$) is larger than in neutral carbene analogues and renders these cations more stable and less electrophilic than acyclic or saturated cyclic diamino phosphenium ions [7c,9].

As compared to the extensive knowledge on carbene complexes with ligands of type **II** [5], the coordination chemistry of the analogous main group compounds **III** is far underdeveloped. Some initial reports on silylene and germylene complexes have been published [10], but the coordination chemistry of cationic nitrogen and phosphorus compounds is, apart from a study of the reactions of diazaphospholenium ions (**III**, $E = P^+$) with Ag^+ [11], largely unexplored.

In this work we report on a study of the reactivity of diazaphospholenium cations towards molybdenum and tungsten carbonyls $[M(bipy)(CO)_3L]$ ($M = Mo$, W; bipy = 2,2′-bipyridine, L = CO, MeCN). Regarding the importance of metal-to-ligand back bonding for the stability and physical and chemical properties of phosphenium complexes [12], the selected metal complexes were chosen in order to provide sufficient back-donation ability. A main focus of the presented work will deal with the characterisation of the interplay between (aromatic) intra-ligand and metal-to-ligand π-donor–acceptor interactions for the stabilisation of the formally electron-deficient phosphenium centre.

2. Results and discussion

2.1. Reactions

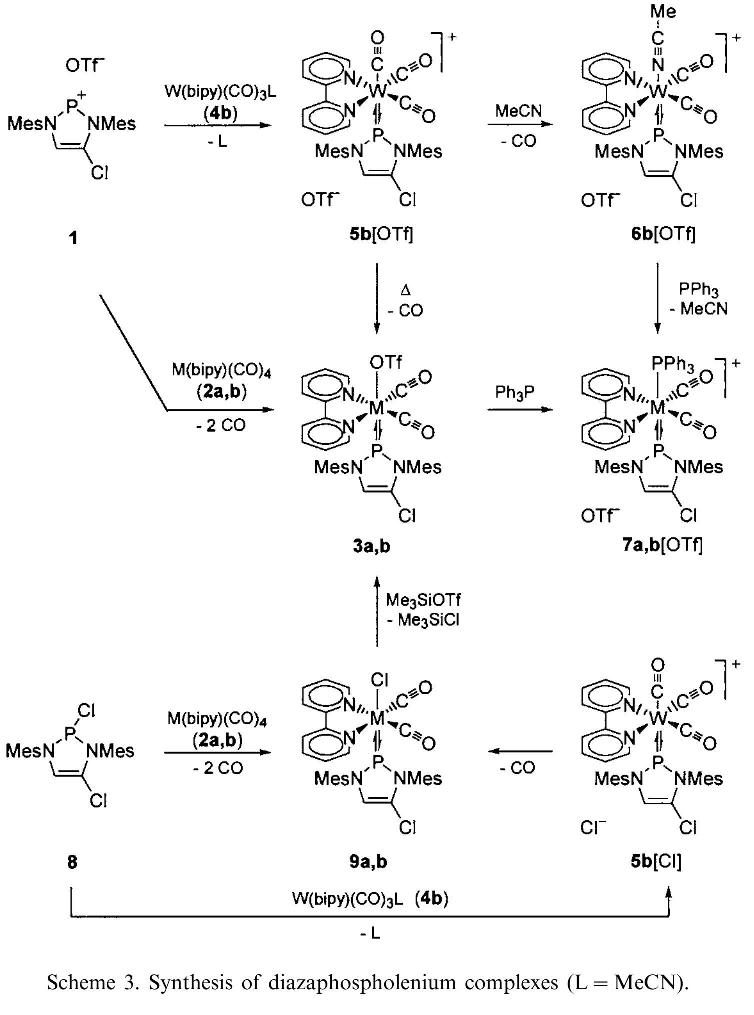
Known synthetic routes to phosphenium complexes [12,13] include direct synthesis from a stable phosphenium ion and a suitable transition metal fragment, metathesis of a phosphanide with a metal halide, or electrophile induced cleavage of an alkoxide from a co-ordinated phosphinite (Scheme 2(a–c)). Base induced dehydrochlorination of complexes with a Cl–P–M–H moiety has been utilised for the generation of neutral phosphenium complexes (Scheme 2(d)) [13]. The formation of cationic complexes by electrophile promoted halide abstraction from coordinated halophosphines (Scheme 2(e), X = F, Cl) which works well in the synthesis of free phosphenium ions [12,13] was successfully demonstrated in the case of $Fe(CO)_4$-complexes [14] but reportedly failed for $W(CO)_5$-complexes [15]. Regarding that the back-donation capability of a $[M(CO_3)(bipy)]$ is larger than that of a $[W(CO)_5]$ fragment and that the *p*-chloro-1,3,2-diazaphospholenes exhibit extraordinarily labile P–Cl bonds [7c,9b,c], we nonetheless thought this approach worth considering, and thus pursued both strategies (a) and (e) for the synthesis of the target complexes.

A survey of the reactions of $[M(bipy)(CO)_3(L)]$ with different available diazaphospholenium salts and *p*-chloro-diazaphospholenes [9c] revealed that complexation occurred only for compounds with *N*-aryl substituents whereas *N*-*tert*-butyl substituted derivatives failed to react. A similar behaviour had been observed previously for the reactions of diazaphospholenium ions with silver salts [10]. Regarding, that variation of the *N*-substituents has only limited effects on structure and bonding in the free cations [9c], this difference in reactivities is presumably of steric rather than of electronic origin.

Successful direct syntheses of diazaphospholenium complexes was achieved by heating toluene suspensions of equimolar amounts of the triflate (**1**) [OTf] [16] and $[M(bipy)(CO)_4]$ (M = Mo (**2a**), W (**2b**). Both reactions proceeded with eventual dissolution of the starting materials and formation of red crystalline precipitates of the triflato complexes **3a**,**b** which were isolated by filtration and characterised by spectroscopic and analytical techniques (see below). Realising that the formation of **3a**,**b** required elimination of two carbonyl ligands from the starting materials, we anticipated that the reaction might proceed in a two step mechanism. To corroborate this hypothesis, we carried out the complexation under milder conditions by reacting **1** [OTf] with $[W(bipy)(CO)_3(MeCN)]$ (**4b**) in CH_2Cl_2 at ambient temperature and obtained a single product which was isolated after evaporation of volatiles and identified spectroscopically as the *fac*-isomer of the tricarbonyl complex **5b** [OTf]. Solutions of **5b** [OTf] in CH_2Cl_2 were stable towards CO elimination up to 40°C, but clean conversion into **3b** was observed upon heating a suspension of the complex in boiling toluene. Refluxing **5b** [OTf] in acetonitrile lead to the quantitative formation of a new product which could not be isolated in analytically pure form, but whose constitution as the cationic nitrile complex **6b** [OTf] was unequivocally established from in situ IR and multinuclear 1D and 2D NMR investigations. A further chemical proof for the postulated constitution was obtained from the reaction with triphenylphosphine which gave the corresponding complex **7b** via selective displacement of the coordinated nitrile and retention of the phosphenium moiety. The same products as well as its molybdenum congener **7a** were alternatively accessible from the reaction of PPh_3 with **3a**,**b** (Scheme 3).

Complexes **2a**,**b** were found to react likewise with the *p*-chloro-diazaphospholene (**8**) in boiling toluene to afford the phosphenium complexes **9a**,**b** with metal–chlorine bonds. Both products precipitated from the reaction mixture and were isolated in good yields after filtration. Again, a transient species was detected and characterised in situ by means of ^{31}P- and ^{183}W-NMR spectroscopy when **8** was reacted with **4b** at ambient temperature in CH_2Cl_2. In contrast to **5b** [OTf], the intermediate was in this case unstable and decomposed slowly to the final product, **9b**, thus precluding all attempts towards its isolation. Based on the similarity of the ^{31}P- and ^{183}W-NMR data with those of **5b** [OTf] (see Table 1), the transient species was assigned as the tricarbonyl complex **5b** [Cl]. The slight differences in δ^{31}P and $^{1}J_{WP}$ between both complexes are due presumably to the stronger nucleophilicity of a chloride as compared to a triflate anion, which leads to ion pairing in solution. This hypothesis was corroborated by the observation that portionwise addition of $[Et_4N][Cl]$ to a CH_2Cl_2 solution of **5b** [OTf] led to a continuous shift of the ^{31}P-NMR signal. Reaction of **9a**,**b** with trimethylsilyl triflate afforded further a quantitative yield of trimethylchlorosilane and the triflate complexes **3a**,**b**.

According to the spectroscopic investigations, all diazaphospholenium complexes exist in solution as a single stereoisomer (the *fac*-isomer for **5b**, and the *trans*-isomers for **3a**,**b**, **6b**, **7a**,**b**, and **9a**,**b**) and showed



Scheme 3. Synthesis of diazaphospholenium complexes (L = MeCN).

Table 1
^{31}P,^{183}W, and IR (νCO) data of complexes [M(**1**)(bipy)(CO)$_2$(L)] in CH_2Cl_2 solution

	M	L	δ^{31}P	$\Delta\delta^{31}$P [a]	δ^{183}W	$^1J_{WP}$ (Hz)	ν(CO) (cm^{-1})
1			205.5				
3a	Mo	OTf	167.0	−38.5			1932, 1853
3b	W	OTf	137.3	−68.2	−1440	770	1921, 1841
5b [OTf]	W	CO	161.8	−43.7	−2105	497	2015, 1932, 1877
5b [Cl]	W	CO	160.1	−45.4	−2100	494	
6b [OTf]	W	MeCN	148.1	−47.4	−1580	707	1911, 1845
7a [OTf]	Mo	PPh_3	172.4 33.7 [b]	−33.1			1917, 1846
7b [OTf]	W	PPh_3	150.0 24.3 [c]	−55.5	−1860	598, 211	1911, 1838
9a	Mo	Cl	145.1	−60.6			1923, 1844
9b	W	Cl	122.3	−83.2	−1680	703	1913, 1834

[a] Coordination shifts: $\Delta\delta^{31}P = \delta^{31}P(\text{complex}) - \delta^{31}P(\mathbf{1})$.

[b] $^2J_{PP} = 207$ Hz.

[c] $^2J_{PP} = 208$ Hz.

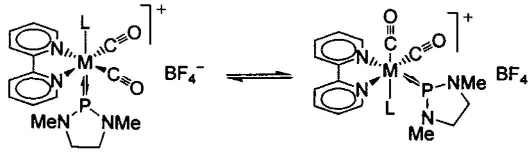
no tendency towards isomerisation to the corresponding *mer*- or *cis*-isomers which had been observed for the complexes **10** containing phosphenium ligands with CC-saturated 5-membered rings (Scheme 4) [17]. For these compounds, the relative stabilities of both stereoisomers were proven to be controlled by a balance of electronic and steric factors [17]: the *mer*/*cis*-isomers gain thermodynamic stability over the corresponding *fac*/*trans* isomers from the tendency of the highly π-acidic phosphenium ligand to occupy a position *trans* to the bipy ligand which exhibits the lowest π-acceptor ability, whereas steric factors enhance the preference of *trans* over *cis* isomers. In view of these findings, the configurational stability of **3**, **5**–**7**, and **9** is presumably attributable to the increased size of the *N*-mesityl-diazaphospholenium units as compared to the *N*-methylated heterocycles in **10**.

The formation of the chloro complexes **9a**,**b** from the *p*-chloro-diazaphospholene (**8**) is remarkable since the P–Cl heterolysis (which was directly observed during the formation of **5b** [Cl] from **8** and **4b**) proceeds spontaneously without support of a Lewis-acid. We relate this unusual reactivity to the combined effects of 'preorganisation' of the ligand **8** due to the presence of an intrinsically weak P–Cl bond, and the strong π-basicity of the metal fragment **4b**. The directing influence of phosphenium substituents to activate a carbonyl ligand in the *trans*-position for substitution by donor ligands of lower π-acidity has been noted previously [17,18].

2.2. Spectroscopic investigations

The constitution of all diazaphospholenium complexes was established from analytical and spectroscopic data. Assignment of the metal stereochemistry was derived in all cases from the ^{13}C-NMR spectra, with the important information being provided by the signals attributable to the CO ligands. Thus, all dicarbonyl complexes displayed only a single resonance, indicating both carbonyl ligands being *trans* to a bipyridine nitrogen atom and thus necessarily *cis* with respect to each other. The *trans*-arrangement of the remaining ligands was in the case of **7a**,**b** further supported by characteristically large values of $^2J_{PP}$ (207–208 Hz) between the phosphorus atoms of the diazaphospholenium and triphenylphosphine ligands which are of similar magnitude as the coupling in the *trans*-isomers of **10c**–**e** [17]. Some compounds displayed a slight broadening of the resonances of the carbonyl as well as the ^{1}H and ^{13}C signals of the bipyridine ligand. Even though the origin of this effect was not elucidated in detail, we take it as indication for the onset of hindered rotation of the diazaphospholenium moiety around the P–M bond which slows down the dynamic interconversion between conformers with different angular orientation of the unsymmetric diazaphospholenium moiety with respect to the M(bipy)(CO)$_2$ set of ligands.

The spectrum of the tricarbonyl complex **5b** displays two carbonyl signals with relative intensities of 1:2. A distinction between *fac*- and *mer*-arrangement of the CO ligands was feasible from the observation of a substantially larger value of $^2J_{PC}$ (84.3 vs. 12.2 Hz) for the less intense signal. This suggested the unique carbonyl ligand to be *trans* to the phosphenium moiety



fac-/trans-**10** *mer-/cis*-**10**

Scheme 4. *Fac*–*mer*/*cis*–*trans* stereoisomerization of phosphenium complexes [17]. (L = CO, M = Mo (**10a**), W (**10b**); L = PPh_3, M = Mo (**10c**); L = 2-methoxy-1,3-dimethyl-1,3,2-diazaphospholidine, M = Mo (**10d**), W (**10e**)).

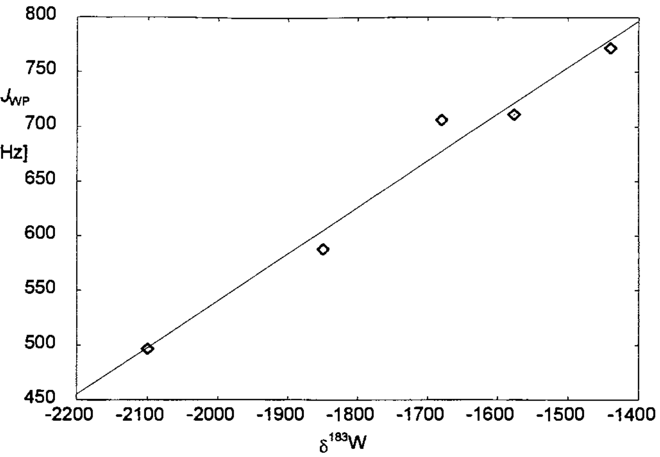


Fig. 1. Correlation between $\delta^{183}W$ and $^1J_{WP}$ for complexes [M(diazaphospholenium)(bipy)$(CO)_2$(L)]. Diamonds denote experimental data; the straight line corresponds to the result of a least-squares fit which gave $^1J_{WP} = 0.426$, $\delta^{183}W + 1393$ with a correlation coefficient $r = 0.987$.

and thus permitted identification of the complex as the *fac*-isomer. This assignment was confirmed by the observation of only one set of resonances for the ^1H and ^{13}C nuclei in both rings of the bipyridine unit which is incompatible with the constitution of a *mer*-isomer featuring one pyridine nitrogen *cis* and the other one *trans* to the phosphenium ligand.

The ^{31}P-NMR data listed in Table 1 reveal negative coordination shifts whose magnitudes ($\Delta\delta = -33$ to -60 for Mo and -44 to -83 for W complexes) exceed those of the phosphenium complexes **10** ($\Delta\delta = -12$ to -20 for Mo and -30 to -42 for W complexes [17]). The $^1J_{^{183}W^{31}P}$ coupling constants are significantly larger than those typically found for phosphine complexes ($^1J_{WP} = 200$–300 Hz; cf. $^1J_{WP} = 211$ Hz for the PPh_3 ligand in **7b**) and match the characteristically large couplings of known phosphenium complexes ($^1J_{WP} = 400$–620 Hz [12,13,17,18]). The coupling in **5b** is larger than in **10b** (M = W, L = CO, $^1J_{WP} = 442$ Hz [17]) and increases further with decreasing π-acidity of the ligand in the *trans*-position in the order of **5b** < **7b** < **6b**, **9b** < **3b**. Comparison of the values of $^1J_{WP}$ and $\delta^{183}W$ which have been obtained from ^{31}P detected ^{31}P, ^{183}W 2D-HMQC spectra [19] reveal a linear correlation between both quantities, with increasing values of $^1J_{WP}$ being accompanied by a deshielding of the metal nucleus. A similar qualitative relation between $^1J_{MoP}$ and $\delta^{95}Mo$ has been reported for a series of complexes [Mo(bipy)(phosphenium)$(CO)_2$(L)]$^+$ (L = phosphites, CO) [20] (Fig. 1).

The observed trends in $^1J_{MP}$ (and δ M) are generally attributed to an increasing degree in M–P double bond character [12,13,17,20]. A rationale for this behaviour can be given by representing the paramagnetic contribution to the magnetic shielding σ^{para} (whose variation dominates the trends in shielding for heavy nuclei) and the reduced spin-spin coupling constants $^1K_{MP}$ ($^1K_{MP} = 4\pi^2/(h\gamma^M\gamma^P)^1J_{MP}$) according to [19b,c]

$$\sigma^{para} \propto (^1\Delta E^{-1})(<r^{-3}>_{np}P_u + <r^{-3}>_{md}D_u)$$

$$^1K_{MP} \propto (^3\Delta E^{-1})s^2(0)_P s^2(0)_M P^2_{MP}$$

where [1,3]ΔE denotes an average electronic excitation energy, $<r^{-3}>$ an orbital expansion term which is related to the nephelauxetic effects, $s(0)_X$ the s-electron density at a nucleus X, and *P*, *D*, p- and d-orbital population terms and bond orders (often summoned to represent the 'imbalance of electron density'), respectively. Even if a concise theoretical analysis is yet lacking, qualitative arguments [17,20] support the assumption that changes in the electronic situation of the phosphorus–metal π-bonding exert a strong influence on both ΔE and the orbital/bond order terms *P*, *D* whose variations dominate presumably the shifts in σ^{para} and K in the structurally closely related molecules considered here. Assuming the validity of these arguments, the observed magnitudes of $^1J_{WP}$ suggest that despite the lower electrophilicity of free **1** with respect to other aminophosphenium ions [9c] the degree of M → L back donation, and thus the phosphorus–metal π-bonding character, in the studied diazaphospholenium complexes is still significant.

In addition to the interpretation of NMR data, comparison of CO stretching frequencies is a well established alternative to assess the π-acidity of co-ligands in mixed carbonyl complexes. Although quantitative analysis is precluded by the unavailability of a complete set of data which would allow concise evaluation of force constants and the inapplicability of concepts such as Tolman's electronic parameter [21], comparison of the νCO frequencies of complexes [M(bipy)$(CO)_2$(L)-(PR_2)]$^+$ which differ only in the R_2P ligand should still provide for a qualitative comparison of the properties of different phosphenium moieties. In fact, comparison of the spectroscopic data of **5b** [OTf] (νCO = 2015, 1932, 1877 cm^{-1}) with those of [17] [W(bipy)$(CO)_3$(1,3-dimethyl-1,3,2-diazaphospholidinium)]$^+$ (**10b**, νCO = 2006, 1920, 1868 cm^{-1}) and [W(bipy)$(CO)_3$ (2-methoxy-1,3-dimethyl-1,3,2-diazaphospholidine)] (**11**, νCO = 1909, 1814, 1790 cm^{-1}) reveals a strong blue shift of νCO for both phosphenium complexes with respect to **11** which reflects the much higher π-acidity of phosphenium as compared to phosphite ligands. The blue shift is slightly larger for **5b** than for **10b**, suggesting that the diazaphospholene **1** is a stronger π-acceptor than the C–C saturated diazaphospholidine ligand in **10b**. The same trend becomes apparent from the comparison of νCO in **7a** [OTf] (νCO = 1917, 1831 cm^{-1}) and [Mo(bipy)$(CO)_2$$(PPh_3)$-(1,3-dimethyl-1,3,2-diazaphospholidinium)]$^+$ (**10c**, νCO = 1909, 1831 cm^{-1} [17]). The higher π-acidity of the cation **1** as compared to the C–C saturated analogue, $[(CH_2NMe)_2P]^+$, is at a first glance surprising in the light of the fact that diazaphospholenium ions are generally much weaker electrophiles than acyclic or saturated cyclic diaminophosphenium ions [7c,9]. However, regarding that introduction of an electron withdrawing Cl substituent at the diazaphospholene ring has been shown to enhance the Lewis acidity of the phosphenium centre [9c], the observed sequence of ligand π-acidities is presumably a consequence of different inductive substituent effects.

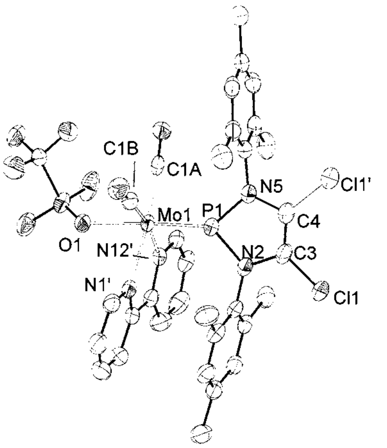


Fig. 2. Molecular structure of **3a** in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, H atoms omitted for clarity; selected bond distances and angles are given in Table 2.

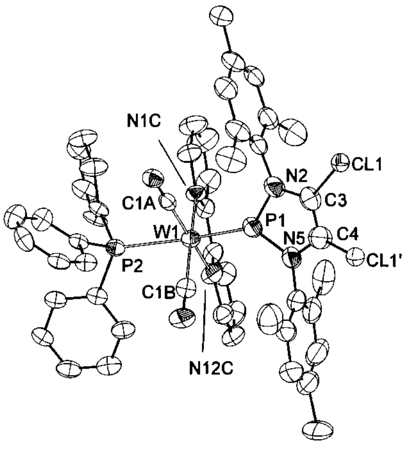


Fig. 3. Molecular structure of the cation **7b** in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, H atoms omitted for clarity; selected bond distances and angles are given in Table 2.

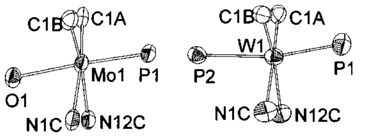


Fig. 4. Representation of the metal coordination spheres in complex **3a** (left) and **7b** (right). C1A, C1B and N1C, N12C denote the ligating carbon and nitrogen atoms of the carbonyl and bipyridine ligands, respectively.

Table 2

Relevant bond lengths (Å) and bond angles (°) of the phosphenium complexes **3a**, **7b** [OTf], **10d**, and the 1,3,2-diazaphospholenium cation **1a** [a]

	3a	**7b** (OTf)	**1** [9c]	**10d** (OTf) [16b]
Bond lengths				
P–N	1.697(4)	1.671(7)	1.6662(15)	1.642(5),
	1.682(4)	1.678(7)	1.6708(15)	1.644(5)
N–C	1.397(6)	1.389(10)	1.374(2)	
	1.404(6)	1.366(9)	1.378(2)	
C=C	1.318(7)	1.303(11)	1.351(2)	
N–C_{exo}	1.436(6)	1.450(9)	1.460(2)	
	1.435(5)	1.438(10)	1.464(2)	
Bond angles				
M–P	2.2016(12)	2.247(2)		2.254(1)
M–C(CO)	1.969(5)	1.956(9)		1.953(6)
	1.964(5)	1.973(9)		1.966(6)
M–N(bipy)	2.230(4)	2.219(6)		2.244(4)
	2.231(4)	2.224(6)		2.255(5)
M–X	2.250(3)	2.543(2)		2.495(1)
P–M–X	176.88(8)	167.80(7)		166.85(5)

[a] N–C_{exo} denotes the exocyclic N–C(mesityl) bond and X the ligating atom of the ligand *trans* to the phosphenium fragment.

2.3. Crystal structure studies

Single crystal structure determinations were carried out for **3a** and **7b** [OTf]. Both crystalline phases contain isolated neutral or cationic complexes, which displayed no unusual short intermolecular distances. In both compounds the Cl atom at the diazaphospholene ring was found to be disordered between two positions with relative occupancy factors of 70:30 (**3a**) and 76:24 (**7b** [OTf]), respectively. We interpret this in terms of a superposition of two different molecules, which differ in the rotational orientation of the diazaphospholene moiety around the P–M bond. Inspection of the final atomic coordinates and anisotropic displacement parameters indicated that the positions of all ring atoms are sufficiently well defined to extract reliable bonding parameters. Drawings of the complexes are depicted in Figs. 2 and 3, respectively, and a reduced representation of the metal coordination environments is given in Fig. 4. Important bond distances are compared with those of the free ligand **1** [9c] and the complex *trans*-**10d** [17b] in Table 2.

Both **3a** and **7b** have distorted octrahedral coordination spheres around the metal atom. The metal lies in one plane with the ligating carbon and nitrogen atoms of the CO and bipy ligands and the remaining M–P and M–O bonds are close to perpendicular to this plane.

The M–C and M–N distances in **3a**, **7b**, and **10d** are indistinguishable within experimental error, in accordance with the assumption of practically identical covalence radii for both Mo and W in the present coordination enviroment. The diazaphospholene rings in both complexes are planar (mean deviations of ring atoms from the best-fit planes are 0.03(0.01) Å) and the sum of valence angles around the P1 atom amounts to 360 (359)° for **3a** (**7b**). The angle between the diazaphospholene ring plane and a line bisecting the C1A–M–C1B angle enclosing the two metal–carbonyl bonds is 21° for **3a** and 102° for **7b**. As a consequence, the relative orientations of the rings, with respect to the remaining ligands in both complexes, are close to orthogonal, reflecting no particular preference for a certain conformation and suggesting that the rotational barrier around the P–M bond may be similarly low as in carbene complexes. The M–P1(phosphenium) distances increase in the order **3a** (2.2016(12) Å) $\ll$ **7b** (2.247(2) Å) $<$ **10d** (2.254(1) Å [17b]) and the observed shortening of the P1–M with respect to the P2(phosphine)–M bond is more pronounced in **7b** (12%) than in **10d** (10% [17b]). These trends are considered to reflect mainly the varying electronic influences of the *trans*-ligands: the presence of a triflate, which is both a weak π-donor and a negligible π-acceptor, leads to distinct contraction of the M–P(phosphenium) bond, and the order of M–P distances in **7b** and **10d** is in accordance with a greater π-accepting power of the phosphite type ligand in **10d** as compared to PPh_3. The pronounced M–P1 bond shortening in combination with the planar phosphorus coordination environment is certainly indicative of considerable M–P double bond character, and, assuming that the structural parameters of **3a** and the analogous tungsten complex **3b** should be similar, corroborates the conclusions derived from the discussion of spectroscopic data.

The P–N, C–N, and C–C bonds in the diazaphospholene rings of **3a** and **7b** are indistinguishable within experimental error. Comparison with the corresponding bond distances of free **1** [9c] (Table 2) reveals a lengthening of P–N and C–N bonds and a slight shortening of the C–C bond, and the observed distances come close to those found for the corresponding 4-chloro-1,3-dimesityl-2-hydrido-1,3,2-diazaphospholene [22] (P–N 1.709(3), 1.722(3), C–N 1.407(5), 1.410(5), C = C 1.327(5) Å) with a pyramidal phosphorus atom. The exocyclic N–C(mesityl) bonds in **3a** and **7b** are slightly shorter than that in **1** so that on the whole, the marked deviation between endocyclic and exocyclic N–C bonds emanating from the same nitrogen atom which was observed for **1** [9c] becomes less pronounced. Comparison of the P–N distances in **3a**, **7b** and **10d** reveals that the bond lengthening associated with the introduction of CC unsaturation in the ring of the free ligand **1** [9c] is further reinforced upon complexation. Altogether, these effects can be interpreted by assuming that the strong M–P π-interaction introduces a massive reduction in cyclic intraligand π-delocalisation. Structure comparisons involving the complexes **7b** and **10d** and the corresponding free phosphenium ligands [23] suggest that the P–N bond weakening which accompanies the development of M–P π-bonding in phosphenium complexes [12,17b] is more pronounced in **3a** and **7b** than in **10d**, again indicating a greater π-accepting power of **1** as compared to the CC-saturated phosphenium ligand in **10d**.

3. Conclusions

Diazaphospholenium complexes are readily accessible from reactions of complexes **2a**,**b** and **4b** with both the cation **1** and the *p*-chloro-diazaphospholene (**8**). The latter reaction involves an unprecedented coordination induced ionisation of P–Cl bonds. In contrast to known phosphenium syntheses, this reaction is promoted by strong M → P charge transfer from the highly π-basic transition metal fragment in combination with a suitable ‘preorganisation’ (due to intrinsic, electronically induced P–Cl bond weakening) of the ligand and requires no further assistance by an external electrophile.

Spectroscopic and structural studies give evidence for the presence of considerable M–P double bond character in the formed complexes which leads to a marked reduction of π-delocalisation in the diazaphospholene ring of the ligand. This suggests a low ‘hardness’ of the diazaphosphenium moiety which is in contradiction with a high degree of aromatic character [24] and gives further support to the results of our previous investigation of this issue [9c]. The structural studies indicate further that, as in the case of carbene complexes, no peculiar preference for a fixed configuration of the formal M–P double bond prevails. Spectroscopic and structural data indicate a higher π-acidity for the diazaphospholenium as compared to a CC-saturated heterocyclic phosphenium ligand which contrasts with the lower electrophilicity of **1** with respect to non-conjugated diaminophosphenium species [9c]. Even if a concise investigation of the origin of this discrepancy has to be postponed to future studies, it is presumably explained by tuning of the ligand electrophilicities by subtle inductive substituent effects [9c].

Last, but not least, the high π-accepting power of a coordinated diazaphospholenium unit facilitates the substitution of ligands in the *trans*-position and allows easy access to reactive phosphenium complexes containing weakly coordinated nitrile or triflate ligands which promise further interesting reactivities.

4. Experimental

4.1. General remarks

All manipulations were carried out under dry argon. Solvents were dried by standard procedures. Compounds **1** [OTf], **8** [9c] **2a**,**b**, **4b** [17], were prepared as described. NMR spectra: Bruker AMX300 (^{1}H, 300.1 MHz; ^{31}P, 121.5 MHz; ^{13}C, 75.4 MHz; ^{183}W, 12.5 MHz) and Bruker AMX500 (^{1}H, 500.1 MHz; ^{13}C, 125.7 MHz); chemical shifts referenced to ext. TMS (^{1}H, ^{13}C), 85% H_3PO_4 ($\Xi = 40.480747$ MHz), aq. WO_4^{2-} ($\Xi = 4.166388$ MHz); ^{183}W chemical shifts were determined from ^{31}P detected ^{31}P-, ^{183}W{^{1}H}-HMQC spectra [19]; positive signs of chemical shifts denote shifts to lower frequencies, and coupling constants are given as absolute values; prefixes *i*-, *o*-, *m*-, *p*- denote atoms of mesityl and phenyl substituents, and atoms in the diazaphospholene ring are denoted as 4-C, 5-H, etc.; assignment of resonances were derived in ambiguous cases from analysis of 2D ^{1}H,^{13}C-HMQC and HMBC, and ^{1}H-,^{31}P-HMQC NMR spectra. MS: Kratos Concept 1H, Xe-FAB, m-NBA matrix-FT-IR spectra: Bruker IFS 113V, in CH_2Cl_2 solution. Elemental analyses: Heraeus CHNO-Rapid. Melting points were determined in sealed capillaries. ^{31}P- and ^{183}W-NMR data as well as IR data are listed in Table 1.

4.2. Preparation of complexes ***9a***,***b***

A solution of **8** (5 mmol) and the appropriate metal complex **2a** or **2b** (5 mmol) in 150 ml of toluene was refluxed for 24 h. After cooling, the formed precipitate was filtered over a glass filter frit and washed with cold toluene. The crude products were purified by recrystallisation from boiling toluene.

trans-[(2,2′-Bipyridine)-dicarbonyl-chloro-(1,3-dimesityl-4-chlorodiazaphospholenium)-molybdenum(0)] (**9a**): yield 95%, m.p. > 260°C. ^{1}H-NMR ($CDCl_3$): 1.94 [s, 6H, *o*-Me], 2.12 [s, 6H, *o*-Me], 2.21 [s, 3H, *p*-Me], 2.26 [s, 3H, *p*-Me], 6.35 [d, $^3J_{PH} = 6.4$ Hz, 1H, 5-H], 6.58 [s, 2H, *m*-H], 6.74 [s, 2H, *m*-H], 7.11 [br, 2H, *m*-H(bipy)], 7.64 [br, 2H, *p*-H(bipy)], 7.69 [br, 2H, *m*-H(bipy)], 8.60 [d, $^3J_{HH} = 4.2$ Hz, 2H, *o*-H(bipy)]. ^{13}C{^{1}H}-NMR ($CDCl_3$): 18.7 [br, *o*-Me], 21.72 [s, *p*-Me], 21.77 [s, *p*-Me], 119.14 [s, 4-C], 120.4 [s, 5-C], 123.2 [s, *m*-CH(bipy)], 125.3 [s, *m*-CH(bipy)], 129.5 [br, *m*-CH], 129.8 [br, *m*-CH], 131.6 [br, *i*-C], 134.6 [br, *i*-C], 137.4 [br, *o*-C], 137.5 [s, *p*-CH(bipy)], 138.2 [br, *o*-C], 139.0 [s, *p*-C], 139.1 [s, *p*-C], 152.6 [s, *o*-CH(bipy)], 155.1 [s, *o*-C(bipy)], 228.2 [d, $^2J_{PC} = 19.4$ Hz, CO]. FAB-MS: *m*/*z* (%): 702 (20) [M$^+$]. Anal. Calc. for $C_{32}H_{31}Cl_2MoN_4O_2P$ (701.4): C, 54.79; H, 4.45; N, 7.99. Found: C, 55.59; H, 4.58; N, 8.11%.

trans-[(2,2′-Bipyridine)-dicarbonyl-chloro-(1,3-dimesityl-4-chlorodiazaphospholenium)-tungsten(0)] (**9b**): yield 86%, m.p. > 260°C. ^{1}H-NMR (CD_2Cl_2): 1.96 [s, 6H, *o*-Me], 2.11 [s, 6H, *o*-Me], 2.22 [s, 3H, *p*-Me], 2.26 [s, 3H, *p*-Me], 6.39 [br, 1H, *m*-H(bipy)], 7.75 [br, 4H, *p*-H(bipy) and *m*-H(bipy)], 8.31 [br, 2H, *o*-H(bipy)]. ^{13}C{^{1}H}-NMR (CD_2Cl_2): 18.1 [br, *o*-Me], 21.0 [s, *p*-Me], 21.1 [s, *p*-Me], 118.8 [s, 4-C], 119.4 [s, 5-C], 123.0 [s, *m*-CH(bipy)], 125.6 [s, *m*-CH(bipy)], 128.9 [s, *m*-CH], 129.1 [s, *m*-CH], 131.4 [d, $^2J_{PC} = 6.0$ Hz, *i*-C], 134.0 [d, $^2J_{PC} = 6.5$ Hz, *i*-C], 137.1 [d, $^3J_{PC} = 2.3$ Hz, *o*-C], 137.2 [s, *p*-CH(bipy)], 138.0 [d, $^3J_{PC} = 2.3$ Hz, *o*-C], 138.3 [d, $^5J_{PC} = 1$ Hz, *p*-C], 138.5 [d, $^5J_{PC} = 1$ Hz, *p*-C], 151.9 [s, *o*-CH(bipy)], 155.3 [s, *o*-C(bipy)], 223.1 [d, 2JPC = 11.4 Hz, CO]. FAB-MS: *m*/*z* (%): 790 (70) [M$^+$]. Anal. Calc. for $C_{32}H_{31}Cl_2N_4O_2PW$ (789.4): C, 48.69; H, 3.96; N, 7.10. Found: C, 46.99; H, 4.08; N, 7.11%.

4.3. Preparation of complexes ***3a***,***b***

(a) A solution of **1** [OTf] (1 mmol) and the appropriate complex **2a** or **2b** (1 mmol) in 30 ml of toluene was refluxed for 24 h. After cooling, the formed precipitate was filtered over a glass filter frit and washed with cold toluene.

(b) Trimethylsilyltriflate (2 mmol) was added dropwise to a cooled (4°C) solution of **9a**,**b** (1 mmol) in 50 ml of CH_2Cl_2. The solution was stirred for 1 h and then allowed to warm to ambient temperature. Volatiles were removed in vacuo, and the remaining residue was washed twice with toluene–hexane (2:1). and added dropwise to 4°C for 24 h. The crude products were purified by recrystallisation from THF at −20°C.

trans-[(2,2′-Bipyridine)-dicarbonyl-(1,3-dimesityl-4-chlorodiazaphospholenium) - triflato - molybdenum(0)] (**3a**): yield 76%, m.p. 242–246°C. ^{1}H-NMR ($CDCl_3$): 1.94 [s, 6H, *o*-Me], 2.09 [s, 6H, *o*-Me], 2.21 [s, 3H, *p*-Me], 2.25 [s, 3H, *p*-Me], 6.43 [d, $^3J_{PH} = 6.6$ Hz, 1H, 5-H], 6.61 [s, 2H, *m*-H], 6.74 [s, 2H, *m*-H], 7.17 [br, 2H, *m*-H(bipy)], 7.75 [br, 4H, *p*-H(bipy) and *m*-H(bipy)], 8.62 [s, 2H, *o*-H(bipy)]. ^{13}C{^{1}H}-NMR ($CDCl_3$): 18.5 [br, *o*-Me], 21.6 [s, *p*-Me], 119.9 [q, $^1J_{FC} = 321$ Hz, CF_3], 120.3 [s, 4-C], 121.5 [s, 5-C], 123.2 [s, *m*-CH(bipy)], 125.9 [s, *m*-CH(bipy)], 129.6 [br, *m*-CH], 129.8 [br, *m*-CH], 130.9 [d, $^2J_{PC} = 5.0$ Hz, *i*-C], 133.9 [d, $^2J_{PC} = 5.7$ Hz, *i*-C], 137.0 [br, *o*-C], 137.9 [br, *o*-C], 138.9 [s, *p*-CH(bipy)], 139.4 [s, *p*-C], 139.6 [s, *p*-C], 152.9 [s, *o*-CH(bipy)], 155.4 [s, *o*-C(bipy)], 228.2 [d, $^2J_{PC} = 21.7$ Hz, CO]. FAB-MS: *m*/*z* (%): 816 (1) [M$^+$], 667 (65) [M$^+$ − OTf]. Anal. Calc. for $C_{33}H_{31}ClF_3MoN_4O_5PS$ (815.0): C, 48.63; H, 3.83; N, 6.87. Found: C, 47.9; H, 3.9; N, 6.8%.

trans-[(2,2′-Bipyridine)-dicarbonyl-(1,3-dimesityl-4-chlorodiazaphospholenium)-triflato-tungsten(0)] (**3b**): yield 72%, m.p. 222–224°C. ^{1}H-NMR ($CDCl_3$): 1.95 [s, 6H, *o*-Me], 2.11 [s, 6H, *o*-Me], 2.21 [s, 3H, *p*-Me], 2.24

[s, 3H, *p*-Me], 6.43 [d, $^3J_{PH} = 7.9$ Hz, 1H, 5-H], 6.61 [s, 2H, *m*-H], 6.74 [s, 2H, *m*-H], 7.23 [br, 2H, *m*-H(bipy)], 7.83 [br, 4H, *p*-H(bipy) and *m*-H(bipy)], 8.70 [br, 2H, *o*-H(bipy)]. $^{13}C\{^1H\}$-NMR ($CDCl_3$): 18.7 [br, *o*-Me], 21.8 [s, *p*-Me], 21.7 [s, *p*-Me], 119.5 [q, $^1J_{FC} = 322$ Hz, CF_3], 120.3 [s, 4-C], 120.7 [s, 5-C], 123.4 [s, *m*-CH(bipy)], 126.6 [s, *m*-CH(bipy)], 129.6 [s, *m*-CH], 129.8 [s, *m*-CH], 130.9 [br, *i*-C], 133.9 [br, *i*-C], 137.4 [br, *o*-C], 138.2 [br, *o*-C], 139.0 [s, *p*-CH(bipy)], 139.2 [s, *p*-C], 139.4 [s, *p*-C], 153.1 [s, *o*-CH(bipy)], 156.4 [s, *o*-C(bipy)], 222.0 [d, $^2J_{PC} = 9.5$ Hz, CO]. FAB-MS: *m*/*z* (%): 753 (40) [$M^+ - OTf$]. Anal. Calc. for $C_{33}H_{31}ClF_3N_4O_5PSW$ (903.0): C, 43.90; H, 3.46; N, 6.20. Found: C, 42.9; H, 3.5; N 6.1% (Table 4).

4.4. Preparation of complexes **7a**,**b** [OTf]

Triphenylphosphine (1 mmol) was added to a solution of **3a** or **3b** (1 mmol) in 50 ml of CH_2Cl_2 and the resulting mixture was stirred for 2 h. After removal of volatiles in vacuo, the remaining residue was triturated three times with hexanes under ultrasonic irradiation. The crude products were purified by recrystallisation from THF–CH_2Cl_2 (1:1) at −20°C.

Table 3
Crystallographic data, structure solution and refinement of **3a** and **7b** (OTf)

	3a	**7b** [OTf]
Molecular formula	$C_{22}H_{31}ClF_3MoN_4O_5PS$	$C_{55}H_{54}ClF_3N_4O_6P_2SW$
Molecular weight	815.04	1237.32
Dimensions (mm)	0.20 × 0.20 × 0.05	0.35 × 0.20 × 0.10
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	Pbca (no. 61)
a (Å)	8.9238(6)	17.9292(9)
b (Å)	10.5219(6)	16.1206(14)
c (Å)	18.6742(10)	39.207(4)
α (°)	94.931(3)	
β (°)	93.141(3)	
γ (°)	91.417(3)	
V (Å^3)	1743.54(18)	11332.1(15)
Z	2	8
ρ (g cm^{-3})	1.552	1.450
μ (mm^{-1})	0.62	2.24
F(000)	828	4992
Diffractometer	Nonius KappaCCD	Nonius KappaCCD
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$
λ (Å)	0.71073	0.71073
Temperature (K)	123(2)	123(2)
2θ max. (°)	50.0	50.0
Index ranges	$-9 \le h \le 9$, $-12 \le k \le 12$, $-22 \le l \le 22$	$-20 \le h \le 16$, $-17 \le k \le 19$, $-46 \le l \le 46$
Measured data	12815	45435
Unique data	5006	8962
R_{int}	0.051	0.075
Refinement	F^2	F^2
Parameters/restraints	458/7	657/656
R for [$I > 2\sigma(I)$]	0.047	0.049
wR_2 (all data)	0.120	0.124
Max./min. difference peak (e Å^{-3})	−0.77/0.73	−0.871/1.564 (near W1)

Table 4
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **3b** (estimated S.D. in parentheses; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor)

	x	*y*	*z*	U_{eq}
S(1)	2956(1)	7828(1)	1238(1)	38(1)
O(1)	3312(3)	6755(3)	1655(2)	36(1)
O(2)	1987(4)	7483(4)	621(2)	58(1)
O(3)	4205(4)	8680(3)	1151(2)	62(1)
C(1)	1745(5)	8764(4)	1805(3)	43(1)
F(1)	2464(3)	9215(3)	2423(2)	68(1)
F(2)	1236(3)	9751(3)	1476(2)	72(1)
F(3)	562(3)	8074(3)	1961(2)	66(1)
Mo(1)	5206(1)	6302(1)	2429(1)	1(1)
C(1A)	5543(5)	8097(5)	2796(2)	35(1)
O(1A)	5679(4)	9156(3)	3010(2)	43(1)
C(1B)	3878(5)	6166(4)	3229(3)	38(1)
O(1B)	3071(4)	6072(3)	3690(2)	51(1)
N(1′)	4679(4)	4386(3)	1852(2)	38(1)
C(2′)	3711(5)	3521(4)	2078(3)	45(1)
C(3′)	3333(6)	2384(5)	1691(3)	55(1)
C(4′)	3928(6)	2107(5)	1044(3)	56(2)
C(5′)	4917(6)	2990(4)	795(3)	48(1)
C(6′)	5264(5)	4120(4)	1202(3)	39(1)
C(7′)	6308(5)	5118(4)	982(2)	38(1)
C(8′)	7135(6)	4951(5)	373(2)	48(1)
C(9′)	8097(6)	5918(5)	205(3)	52(1)
C(10′)	8202(5)	7036(5)	633(3)	43(1)
C(11′)	7359(5)	7143(4)	1232(2)	37(1)
N(12′)	6438(4)	6217(3)	1419(2)	34(1)
P(1)	7109(1)	5793(1)	3138(1)	33(1)
N(2)	8281(4)	4546(3)	3120(2)	38(1)
C(3)	9370(6)	4641(5)	3690(2)	47(1)
Cl(1)	10 569(2)	3388(1)	3788(1)	55(1) [a]
C(4)	9265(6)	5686(5)	4124(3)	48(1)
Cl(1′)	10 571(10)	6521(8)	4777(4)	51(2) [b]
N(5)	8076(4)	6425(3)	3889(2)	37(1)
C(6)	8206(5)	3529(4)	2554(2)	35(1)
C(7)	9062(5)	3660(4)	1958(2)	37(1)
C(8)	8945(5)	2685(4)	1415(2)	38(1)
C(9)	7996(5)	1625(4)	1448(2)	37(1)
C(10)	7202(5)	1538(4)	2056(2)	40(1)
C(11)	7286(5)	2474(4)	2615(2)	39(1)
C(12)	10 052(5)	4830(5)	1911(3)	47(1)
C(13)	7840(6)	607(4)	828(2)	48(1)
C(14)	6389(6)	2361(5)	3276(2)	51(1)
C(15)	7766(5)	7610(4)	4284(2)	35(1)
C(16)	8436(5)	8727(5)	4094(2)	40(1)
C(17)	8196(6)	9850(5)	4505(3)	50(1)
C(18)	7325(6)	9889(5)	5094(3)	53(1)
C(19)	6667(6)	8752(5)	5268(3)	51(1)
C(20)	6855(5)	7589(5)	4876(2)	41(1)
C(21)	9372(6)	8751(5)	3452(3)	56(1)
C(22)	7053(7)	1123(6)	5530(4)	84(2)
C(23)	6120(6)	6379(5)	5062(3)	55(1)

[a] s.o.f. = 0.699(3).

[b] s.o.f. = 0.301(3).

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **7b** [OTf] (estimated S.D in parentheses; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor)

	x	y	z	U_{eq}
W(1)	4780(1)	4530(1)	1564(1)	35(1)
C(1A)	3933(4)	4003(5)	1793(2)	34(2)
O(1A)	3448(3)	3666(3)	1939(1)	43(2)
C(1B)	4237(4)	5581(5)	1493(2)	39(2)
O(1B)	3960(3)	6221(3)	1461(1)	51(2)
N(1C)	5614(4)	3527(4)	1634(2)	38(2)
C(2C)	5460(5)	2788(5)	1757(2)	55(2)
C(3C)	5972(5)	2170(6)	1794(2)	70(3)
C(4C)	6700(6)	2338(6)	1715(3)	81(3)
C(5C)	6872(5)	3094(6)	1596(2)	58(3)
C(6C)	6336(5)	3694(5)	1554(2)	39(2)
C(7C)	6477(5)	4529(6)	1411(2)	43(2)
C(8C)	7178(5)	4803(6)	1303(2)	54(2)
C(9C)	7248(5)	5542(6)	159(2)	63(3)
C(10C)	6631(5)	6044(6)	1103(2)	58(2)
C(11C)	5942(5)	5735(5)	1200(2)	45(2)
N(12C)	5855(4)	5006(4)	1360(2)	48(2)
P(1)	4272(1)	4089(1)	1073(1)	45(1)
N(2)	3786(4)	3251(4)	956(2)	56(2)
C(3)	3482(6)	3359(6)	633(2)	78(3)
Cl(1)	3006(2)	2566(2)	441(1)	96(1) [a]
C(4)	3650(5)	4059(6)	485(2)	68(3)
Cl(1′)	3107(6)	4337(7)	147(3)	96(1) [b]
N(5)	4090(4)	4528(4)	694(2)	50(2)
C(6)	3670(5)	2510(5)	1159(2)	43(2)
C(7)	3015(5)	2403(6)	1328(2)	52(2)
C(8)	2916(5)	1645(6)	1498(2)	54(2)
C(9)	3425(5)	1038(6)	1505(2)	52(2)
C(10)	4077(5)	1157(5)	1334(2)	53(2)
C(11)	4227(5)	1890(6)	1150(2)	54(2)
C(12)	2400(4)	3061(5)	1308(2)	71(3)
C(13)	3260(5)	222(5)	1679(2)	73(3)
C(14)	4933(4)	1978(6)	946(3)	79(3)
C(15)	4385(6)	5313(6)	585(2)	56(2)
C(16)	5117(6)	5358(7)	464(2)	63(2)
C(17)	5360(6)	6132(7)	352(2)	5(3)
C(18)	4898(8)	6820(8)	356(3)	96(4)
C(19)	4197(7)	6758(6)	486(2)	83(3)
C(20)	3894(6)	6010(6)	600(2)	61(2)
C(21)	5591(5)	4606(6)	448(2)	91(3)
C(22)	5128(7)	7681(6)	193(3)	39(5)
C(23)	3120(5)	5937(6)	723(2)	89(3)
P(2)	5071(1)	5012(1)	2168(1)	34(1)
C(21A)	5664(4)	4260(4)	2392(2)	31(2)
C(22A)	6416(4)	4383(4)	2425(2)	36(2)
C(23A)	6860(5)	3812(5)	2578(2)	50(2)
C(24A)	6557(5)	3076(5)	2695(2)	51(2)
C(25A)	5837(5)	2928(5)	2656(2)	58(3)
C(26A)	5359(4)	3499(5)	2501(2)	52(2)
C(21B)	5577(4)	5986(5)	2241(2)	30(2)
C(22B)	5781(4)	6218(4)	2573(2)	37(2)
C(23B)	6192(4)	6956(5)	2623(2)	38(2)
C(24B)	6366(4)	7454(5)	2356(2)	45(2)
C(25B)	6125(4)	7238(5)	2034(2)	45(2)
C(26B)	5716(4)	6517(5)	1974(2)	44(2)
C(21C)	4256(4)	5145(4)	2446(2)	30(2)
C(22C)	3659(4)	5587(4)	2328(2)	39(2)
C(23C)	3041(4)	5755(4)	2526(2)	41(2)
C(24C)	3010(4)	5474(5)	2847(2)	47(2)
C(25C)	3604(5)	5011(5)	2981(2)	54(2)
C(26C)	4228(4)	4875(5)	2780(2)	43(2)
S(1)	5814(2)	9003(2)	1124(1)	86(1)
O(1)	6356(3)	8575(4)	1332(2)	84(2)
O(2)	5853(4)	8890(6)	775(2)	148(3)
O(3)	5689(5)	9873(5)	1226(2)	145(3)
C(1)	4978(5)	8492(8)	1242(3)	72(3)
F(1)	4979(3)	7704(4)	1190(2)	120(2)
F(2)	4829(3)	8618(5)	1567(2)	116(2)
F(3)	4389(3)	8775(4)	1071(2)	114(2)
O(1T)	2097(6)	4727(6)	153(3)	134(3) [a]
C(1T)	1579(8)	4524(9)	433(4)	132(4) [a]
C(2T)	1026(8)	5136(10)	405(4)	133(4) [a]
C(3T)	965(8)	5178(10)	48(4)	146(4) [a]
C(4T)	1653(9)	5188(10)	−94(4)	139(4) [a]
O(2T)	2263(17)	1982(19)	−689(9)	134(3) [b]
C(5T)	1950(2)	2750(2)	−792(9)	126(4) [b]
C(6T)	1720(2)	3100(2)	−495(11)	129(4) [b]
C(7T)	1610(2)	2450(3)	−275(9)	131(4) [b]
C(8T)	2220(2)	1940(2)	−317(9)	131(4) [b]

[a] s.o.f. = 0.756(3).
[b] s.o.f. = 0.244(3).

trans-[(2,2′-Bipyridine)-dicarbonyl-(1,3-dimesityl-4-chlorodiazaphospholenium)-triphenylphosphine-molybdenum(0)] triflate (**7a**): yield 82%, m.p. 226–228°C. ^{1}H-NMR ($CDCl_3$): 1.92 [s, 6H, *o*-Me], 2.01 [s, 6H, *o*-Me], 2.3 [br, 6H, *p*-Me], 6.64 [d, $^3J_{PH} = 5.3$ Hz, 1H, 5-H], 6.81 [s, 2H, *m*-H], 6.86 [s, 2H, *m*-H], 6.9-7.2 [m, 15H, PPh_3], 7.22 [br, 2H, *m*-H(bipy)], 7.75 [br, 2H, *p*-H(bipy)], 7.84[m, 2H, *m*-H(bipy)], 8.31 [br, 2H, *o*-H(bipy)]. $^{13}C\{^1H\}$-NMR ($CDCl_3$): 18.3 [br, *o*-Me], 18.4 [br, *o*-Me], 21.6 [s, *p*-Me], 21.7 [s, *p*-Me], 121.5 [q, $^1J_{FC} = 321$ Hz, CF_3], 122.2 [s, 4-C], 123.2 [s, 5-C], 123.3 [s, *m*-CH(bipy)], 125.7 [s, *m*-CH(bipy)], 129.0 [s, *m*-CH], 129.1 [s, *m*-CH], 130.1 [d, $^3J_{PC} = 6.5$ Hz, *m*-CH(PPh_3)], 130.4 [d, $^4J_{PC} = 1.9$ Hz, *p*-CH(PPh_3)], 130.4 [br, *i*-C], 131.1 [d, $^1J_{PC} = 34.5$ Hz, *i*-C(PPh_3)], 133.1 [d, $^2J_{PC} = 11$ Hz, *o*-CH(PPh_3)], 133.4 [d, $^2J_{PC} = 6.1$ Hz, *i*-C], 136.6 [d, $^2J_{PC} = 3.1$ Hz, *o*-C], 137.5 [d, $^2J_{PC} = 3.1$ Hz, *o*-C], 139.1 [s, *p*-CH(bipy)], 140.2 [s, *p*-C], 140.5 [s, *p*-C], 152.6 [s, *o*-CH(bipy)], 154.3 [s, *o*-C(bipy)], 225.0 [dd, $^2J_{PC} = 12.8$ Hz, 18.9 Hz, CO]. FAB-MS: m/z (%): 929 (35) [$M^+ - OTf$], 667 (75) [$M^+ - OTf - PPh_3$]. Anal. Calc. for $C_{51}H_{46}ClF_3MoN_4PO_5S$ (1046.4)·2THF: C 58.01 H 5.12 N 4.59; Found C 57.50 H 5.0 N 4.55%.

trans-[(2,2′-Bipyridine)-dicarbonyl-(1,3-dimesityl-4-chlorodiazaphospholenium)-triphenylphosphine-tungsten(0)] triflate (**7a**): yield 71%, m.p. 212–214°C. ^{1}H-NMR (CD_2Cl_2): 1.93 [s, 6H, *o*-Me], 2.02 [s, 6H, *o*-Me], 2.33 [br, 6H, *p*-Me], 6.71 [d, $^3J_{PH} = 5.9$ Hz, 1H, 5-H], 6.83 [s, 2H, *m*-H], 6.86 [s, 2H, *m*-H], 6.9-7.2 [m, 15H, PPh_3], 7.3-8.2 [8H (bipy)]. $^{13}C\{^1H\}$-NMR (CD_2Cl_2): 17.9 [br, *o*-Me], 18.1 [br, *o*-Me], 21.1 [s, *p*-Me], 21.2 [s, *p*-Me], 120.9 [q, $^1J_{FC} = 320$ Hz, CF_3], 122.0 [s, 5-C], 122.7 [s, 4-C], 123.8 [s, *m*-CH(bipy)], 125.5 [s, *m*-CH(bipy)], 128.8 [s, *m*-CH], 128.9 [s, *m*-CH], 129.8 [d, $^{3}JPC = 5.3$ Hz, *m*-CH(PPh$_3$)], 130.1 [br, *i*-C], 130.4 [d, $^{4}J_{PC} = 1.9$ Hz, *p*-CH(PPh$_3$)], 131.3 [d, $^{1}J_{PC} = 42$ Hz, *i*-C(PPh$_3$)], 133.1 [d, $^{2}J_{PC} = 10.7$ Hz, *o*-CH(PPh$_3$)], 135.1 [d, $^{3}J_{PC} = 3.4$ Hz, *o*-C], 135.2 [br, *i*-C], 137.7 [d, $^{3}J_{PC} = 3.1$ Hz, *o*-C], 138.1 [s, *p*-CH(bipy)], 139.9 [d, $^{5}J_{PC} = 1.1$ Hz *p*-C], 140.2 [d, $^{5}J_{PC} = 1.1$ Hz, *p*-C], 152.7 [s, *o*-CH(bipy)], 154.9 [s, *o*-C(bipy)], 218.1 [dd, $^{2}J_{PC} = 12.4$ Hz, 9.3 Hz, CO]. FAB-MS: *m*/*z* (%): 929 (35) [$M^{+} - OTf$], 667 (75) [$M^{+} - OTf$, –PPh$_3$]. Anal. Calc. for $C_{51}H_{46}ClF_3N_4PO_5SW$ (1134.3)·2THF: C, 55.43; H, 4.89; N, 4.38. Found: C, 54.56; H, 4.95; N, 4.31% (Table 5).

4.5. Preparation of *fac*-[(2,2′-bipyridine)-tricarbonyl-(1,3-dimesityl-4-chlorodiazaphospholenium)-tungsten(0)] triflate (**5b**) [OTf]

A solution containing **1** [OTf] (1 mmol) and **4b** (1 mmol) in 20 ml of CH_2Cl_2 was stirred for 1 h at ambient temperature. After removal of volatiles in vacuo, the residue was digerated with 10 ml of toluene, and filtered. The resulting crude product was washed several times with toluene and ether. Yield 65%, m.p. 145–147°C. ^{1}H-NMR (CD_2Cl_2): 1.90 [s, 6H, *o*-Me], 1.98 [s, 6H, *o*-Me], 2.37 [br, 6H, *p*-Me], 6.63 [d, $^{3}J_{PH} = 7$ Hz, 1H, 5-H], 6.91 [s, 2H, *m*-H], 6.93 [s, 2H, *m*-H], 7.34 [m, 2H, *m*-H(bipy)], 8.16 [m, 2H, *p*-H(bipy)], 8.43 [m, 4H, *o*-H(bipy)]. ^{13}C{^{1}H}-NMR (CD_2Cl_2): 17.7 [br, *o*-Me], 17.9 [br, *o*-Me], 21.1 [s, *p*-Me], 21.2 [s, *p*-Me], 121.2 [q, $^{1}J_{FC} = 321$ Hz, CF$_3$], 124.3 [s, 4-C], 124.8 [s, *m*-CH(bipy)], 125.1 [s, 5-C], 127.3 [s, *m*-CH(bipy)], 128.9 [br, *i*-C], 130.1 [s, *m*-CH], 130.2 [s, *m*-CH], 131.9 [d, $^{2}J_{PC} = 4.6$ Hz, *i*-C], 137.0 [d, $^{3}J_{PC} = 3.8$ Hz, *o*-C], 138.0 [d, $^{3}J_{PC} = 4.2$ Hz, *o*-C], 139.9 [s, *p*-CH(bipy)], 141.0 [d, $^{5}J_{PC} = 1.5$ Hz, *p*-C], 141.1 [d, $^{5}J_{PC} = 1.5$ Hz, *p*-C], 152.9 [s, *o*-CH(bipy)], 155.4 [s, *o*-C(bipy)], 198.5 [d, $^{2}J_{PC} = 84.3$ Hz, CO], 209.2 [d, $^{2}J_{PC} = 12.2$ Hz, CO]. FAB-MS: *m*/*z* (%): 781 (15) [$M^{+} - OTf$], 753 (30) [$M^{+} - OTf$, –CO].

4.6. Preparation of *trans*-[(acetonitrile)-(2,2′-bipyridine)-dicarbonyl-(1,3-dimesityl-4-chlorodiazaphospholenium)-tungsten(0)] triflate (**6b**) [OTf]

Refluxing a solution of **5b** [OTf] for 30 min in [D$_3$]-MeCN resulted in quantitative formation (^{31}P-NMR control) of a new product identified in situ as **6b** [OTf]. Attempts towards isolating the product by removal of the solvent in vacuo resulted in partial decomposition, presumably with formation of **3b**. ^{1}H-NMR (CD_3CN): 1.98 [s, 6H, *o*-Me], 2.10 [s, 6H, *o*-Me], 2.30 [br, 6H, *p*-Me], 6.74 [s, 2H, *m*-H], 6.81 [s, 2H, *m*-H], 6.83 [d, $^{3}J_{PH} = 8$ Hz, 1H, 5-H], 7.50 [m, 2H, *m*-H(bipy)], 8.13 [br, 4H, *p*-H(bipy) and *m*-H(bipy)], 8.75 [m, 4H, *o*-H(bipy)]. ^{13}C{^{1}H}-NMR (CD_3CN): 17.8 [s, *o*-Me], 17.9 [s, *o*-Me], 20.4 [s, *p*-Me], 20.6 [s, *p*-Me], 120.5 [s, 4-C], 121.4 [q, $^{1}J_{FC} = 321$ Hz, CF$_3$], 122.3 [s, 5-CH], 124.0 [s, *m*-CH(bipy)], 125.3 [s, CN], 127.3 [s, *m*-CH(bipy)], 129.4 [s, *m*-CH], 129.5 [s, *m*-CH], 130.4 [d, $^{2}J_{PC} = 5$ Hz, *i*-C], 133.3 [d, $^{2}J_{PC} = 6$ Hz, *i*-C], 137.1 [d, $^{3}J_{PC} = 2$ Hz, *o*-C], 137.9 [d, $^{3}J_{PC} = 2$ Hz, *o*-C], 138.0 [s, *p*-C], 139.4 [s, *p*-CH(bipy)], 140.4 [s, *p*-C], 152.9 [s, *o*-CH(bipy)], 156.0 [s, *o*-C(bipy)], 219.7 [d, $^{2}J_{PC} = 10.2$ Hz, CO].

4.7. Reaction of the *p*-chloro-diazaphospholene (**8**) with **4b**

A solution containing **1** [OTf] (1 mmol) and **4b** (1 mmol) in 20 ml of CH_2Cl_2 was stirred for 30 min at ambient temperature. An ^{31}P-NMR spectroscopic assay revealed the presence of a mixture of **5b** [Cl] and **9b** beside unreacted **8**. For longer reaction times, increasing conversion of **5b** and **8** into **9b** was observed. Attempts towards isolation of **5b** [Cl] were unsuccessful.

4.8. Crystal structure determinations of compounds **3a** and **7b** [OTf]

The data were collected on a Nonius KappaCCD diffractometer at −150°C using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) [25a]. The non-hydrogen atoms were refined anisotropically, H atoms were refined using a riding model (full-matrix least-squares refinement on F^2 (SHELXL-97) [25b]. In both compounds, the chlorine atom attached to the diazaphospholene ring was disordered between two positions with relative occupancy factors of 85:15 (**3a**) and 76:24 (**7b** [OTf]), respectively. Crystals of **7b** [OTf] contained two additional solvent molecules (THF). Details of data collection and refinement are given in Table 3.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 148149 (**3a**) and CCDC 148150 (**7b** [OTf]), respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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