Tungsten Carbonyl Complexes of 1*H*-Diphosphirenes and Diphosphirenylium Salts

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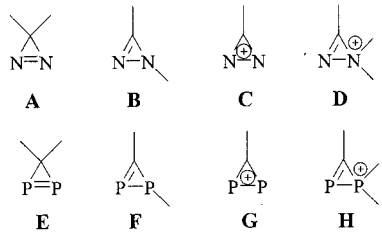
The 1,1,3-tris(diisopropylamino)diphosphirenium salt **1** reacts with lithium aluminium hydride leading to the *P*-hydrogeno-*C*-phosphinophosphaalkenes **2**, which on treatment with a catalytic amount of $BF_3{\cdot}OEt_2$ afford the 1,3-bis(diisopropylamino)-1*H*-diphosphirene **3**. The corresponding η^1-coordinated 1*H*-diphosphirene **6** can be prepared by treatment of **2** or **3** with one equivalent of $[W(CO)_5(thf)]$. Alternatively, the diphosphirenium salt **1** reacts with an excess of $[W(CO)_5(thf)]$, affording the corresponding η^1-coordinated diphosphirenium salt complex **4**, which is converted into the *P*-hydrogenophosphaalkene complex **5** with lithium aluminium hydride. The dinuclear tungsten complexes **7** and **8** are obtained by treatment of the free 1*H*-diphosphirene **3** with two equivalents of $[W(CO)_5(thf)]$ or one equivalent of $[W(CO)_4(thf)_2]$, respectively. Compound **6** reacts with two equivalents of hydrogen chloride, giving the 1-chloro-3-diisopropylamino-1*H*-diphosphirene **9**, which can be subsequently converted into the 1-diisopropylamino-, 1-azido, or 1-phenyl-3-diisopropylamino-1*H*-diphosphirenes **6**, **10** and **11** by nucleophilic substitution with diisopropylamine, azidotrimethylsilane or sodium tetraphenylborate, respectively. The [η^2-(3-diisopropylaminodiphosphirenylium salt)·$W(CO)_5$] complexes **12a-c** can be prepared by reaction of **9** with silver trifluoromethanesulfonate, aluminium or gallium trichloride or, alternatively, by treatment of **6** with two equivalents of trifluoromethanesulfonic acid. Reaction of **12a** with diisopropylamine, water, bis(triphenylphosphoranylidene)-ammonium chloride or tetrabutylammonium fluoride gives the corresponding 1*H*-diphosphirene complexes **6**, **13**, **9**, or **14**, respectively. Compound **12a** also reacts with one or two equivalents of $[W(CO)_5(thf)]$, leading to the di- and trinuclear complexes **15** and **16**, respectively.

Introduction

Three-membered rings, in particular the dinitrogen- and diphosphorus-containing unsaturated heterocycles **A**−**H** (Scheme 1), are not only fascinating species for scientists because of their inherent ring strain, but also valuable starting materials. The chemistry of the 3*H*-diazirines **A**, which are good precursors for transient carbenes, has been extensively explored,[1] whereas only one anti-aromatic 1*H*-diazirine **B** has been spectroscopically characterized.[2] In contrast, for the analogous phosphorus-containing series, one 1*H*-diphosphirene, **F**, has been isolated,[3] while no 3*H*-diphosphirenes **E**, which feature a weak P=P bond,[4] have been characterized.[5] As far as cationic derivatives are concerned,[6] none of the nitrogen-containing systems **C** or **D** has been observed and even the postulated involvement[7] of diazirinium salts, **C**, in the exchange reaction of nucleophiles with halodiazirines has been refuted.[8] The replacement of nitrogen atoms by phosphorus centres decreases the ring strain, and a diphosphirenium salt **H**[9] has been isolated.[10]

Although no complexes featuring 1*H*-diazirines **B** or diazirinium salts **C** and **D** as ligands are known, the coordination chemistry of 3*H*-diazirines **A** constitutes a well-established field in organometallic chemistry.[1c] It is important to note that the cyclic diazirine moiety is retained when bound to group VI metal carbonyls; the diazirine adopts an end-on coordination mode and both mono- and dimetallic complexes have been obtained.

For the diphosphorus-containing series, only two complexes of 1*H*-diphosphirenes **F** have been reported.[11] Here we report experimental and theoretical results concerning the coordination chemistry of heterocycles **F**−**H**. We have evidence for various coordination modes of the 1*H*-diphosphirenes **F** and diphosphirenylium salt **G** to the $W(CO)_5$ fragment.



Scheme 1. Structure of dinitrogen- and diphosphorus-containing heterocycles **A**−**H**

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Results and Discussion

Synthesis of Free and Coordinated 1*H*-diphosphirenes

We have already[12] shown that the 1*H*-diphosphirene **3** is readily available (52% yield) from the diphosphirenium salt **1**[9] via the *P*-hydrogeno phosphaalkenes **2** (Scheme 2). Single crystals of **2**, suitable for an X-ray diffraction study, were obtained from a pentane solution at −20°C (Figure 1, Table 1). The asymmetric unit contains two independent molecules of **2**. Although Fourier synthesis reveals a disorder for the phosphorus-bonded hydrogen atom positions, it is quite clear that both *cis* and *trans* isomers are present in the solid state. The P1−C1−N3−P2−H fragment is nearly planar (average torsion angle: 10°). The planar geometry around N3 (sum of the angles 359.7°), along with the shortness of the C1−N3 bond [1.368(2) Å], suggests an interaction between the nitrogen lone pair and the π system of the P−C bond. This is corroborated by the value of the central C1−P2 bond length [1.713(2) Å], which is at the upper limit for localized C=P double bonds (1.71 Å)[13] although significantly shorter than in HP=C(NMe$_2$)$_2$ [1.740(1) Å].[14] Finally, probably due to severe steric constraints around C1, the C1−P1 bond is elongated [1.899(2) Å] relative to the expected value for a P−C single bond (1.83−1.84 Å).[15]

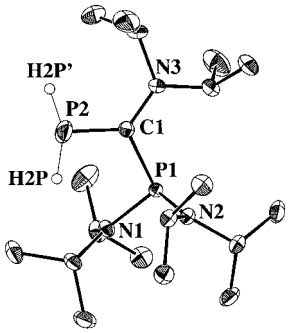


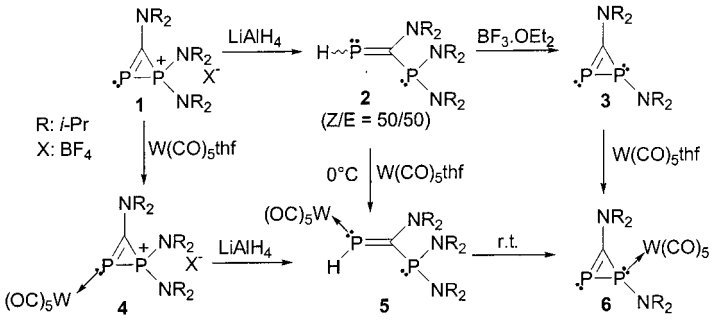
Figure 1. Thermal ellipsoid diagram (30% probability) of **2** showing the atom numbering scheme. Both positions for the disordered hydrogen atom are represented. Selected bond lengths (A) and bond angles (°): P1−C1 1.899(2), P1−N1 1.685(2), P1−N2 1.687(2), C1−N3 1.368(2), C1−P2 1.713(2), P2−H2P 1.226, P2−H2P′ 1.206; P1−C1−N3 114.5(1), P1−C1−P2 118.7(1), N3−C1−P2 126.5(1), C1−P2−H2P 103.2, C1−P2−H2P′ 110.0.

The coordinated 1*H*-diphosphirene **6** can be easily obtained in 65% yield by treatment of **3** with [W(CO)$_5$(thf)]. The end-on coordination of the σ^3-phosphorus centre to the pentacarbonyltungsten fragment was clearly established from the characteristic[16] ^1J(P,W) coupling constant of 295 Hz. Interestingly, **6** can also be prepared directly from phosphaalkenes **2** in 80% yield (Scheme 2). In this case, evidence for the transient formation of the phosphaalkene complex **5** (*E* isomer) has been provided by ^{31}P NMR spectroscopy at 0°C.[12] The metal fragment can even be introduced at the σ^2-phosphorus atom of the diphosphirenium salt **1**. Indeed, treatment of **1** with an excess of [W(CO)$_5$(thf)] in THF at room temperature quantitatively leads to complex **4**. Due to the lability of the P-W bond, this compound was only characterized by ^{31}P NMR spectroscopy [δ = −33.9 (d, *J*(P,P) = 130 Hz, P$^+$), +39.9 (d, *J*(P,P) = 130 Hz, ^1J(P,W) = 249 Hz, σ^{2}P)]. It is noteworthy that the reduction of the coordinated diphosphirenium salt **4** with lithium aluminium hydride affords the coordinated *P*-hydrogeno phosphaalkene **5** (Scheme 2).

Table 1. Crystallographic data for compounds **2** and **8**.

	2	**8**
Chem. formula	$C_{19}H_{43}N_3P_2$	$C_{17}H_{28}ClN_2O_4P_2W$
fw	375.50	611.66
Cryst. syst.	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_12_12$
a, Å	14.641(1)	13.480(3)
b, Å	21.573(2)	18.390(4)
c, Å	16.302(1)	10.303(2)
β, deg	114.51(1)	90
V, Å^3	4685.0(6)	2554.1(9)
F(000)	1664	1200
Z	8	4
D_{calc}, g cm^{-3}	1.065	1.591
T [K]	198	193
μ (Mo-K_α), mm^{-1}	0.192	4.774
2θ range, deg	5−46	5.4−45.4
no. of data collected	27536	10010
no. of unique data	6502	3296
R(int)	0.0663	0.0704
no. of parameters varied	473	261
Goodness-of-fit	1.034	0.971
*R*1	0.0364	0.0471
*wR*2	0.0969	0.1114
$(\Delta/\rho)_{max}$,	0.191	0.976
$(\Delta/\rho)_{min}$, eÅ^{-3}	−0.360	−1.169

Clearly, the reduction/cyclisation sequence can be achieved with free compounds or in the coordination sphere of the tungsten, and the diphosphirenium salt **1** can thereby be converted into the corresponding 1*H*-diphosphirene complex **6**. Moreover, these new synthetic routes can be used on multi-gram scales allowing for the development of the chemistry of 1*H*-diphosphirenes.

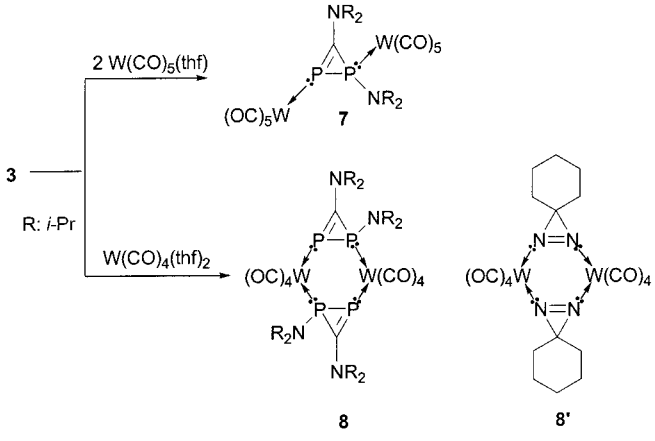


Scheme 2. Synthesis of the mononuclear diphosphirene complex **6**

In **6**, the tungsten is coordinated to the σ^3-phosphorus atom.[17] However, the σ^2-phosphorus atom can also be implicated in the coordination of a transition metal. Indeed, the dinuclear complex **7** is obtained in near quantitative yield when a two-fold excess of [W(CO)$_5$(thf)] is used (Scheme 3). Derivative **7** has been isolated as yellow crystals (mp. 128−129°C) and fully characterized. The coordination of both phosphorus centres is clearly established by ^{31}P NMR spectroscopy {δ = −86.9 [d, *J*(P,P) = 111 Hz, ^1J(P,W) = 296 Hz, P−NR$_2$], −6.3 [d, *J*(P,P) = 111 Hz,

^1J(P,W) = 209 Hz, P=C]}. The IR spectrum features characteristic $\tilde{\nu}_{CO}$ absorption bands at 1934, 1972, 2067 and 2079 cm^{-1}. Among them, the band at 2067 cm^{-1} can be assigned to the $(R_2N)P-W(CO)_5$ fragment by comparison with that observed for the mononuclear complex **6** (2069 cm^{-1}). The absorption at 2079 cm^{-1} can similarly be assigned to the $W(CO)_5$ moiety bonded to the σ^2-phosphorus atom, which suggests a stronger π back donation.[18]

In the nitrogen-containing series, the related 3*H*-diazirines have been used as "structurating" 1,2-bidentate ligands to prepare an original dinuclear double-bridged complex **8′**.[19] This derivative, in which two 3*H*-diazirines coordinate two $W(CO)_4$ fragments, is organised around a *planar* six-membered dimetallacycle. The free 1*H*-diphosphirene **3** was analogously treated with one equivalent of $[W(CO)_4(thf)_2]$.[20] After displacement of the two labile ligands, the dinuclear double-bridged complex **8** was isolated as yellow crystals (M.p. 166−167°C) in 60% yield (Scheme 3). The dimeric structure of **8** was indicated by an A_2B_2 spin system present in the ^{31}P NMR spectrum [δ = −129.4 (P−NR_2), −28.6 (P=C)]. Single crystals of **8**, suitable for an X-ray diffraction study, were grown from a dichloromethane/pentane solution at −20°C. In the solid state (Figure 2), complex **8** is organised around a twofold axis, the six-membered ring adopts an unusual slightly distorted *boat conformation*, and the two three-membered rings occupy equatorial positions. The geometry of the 1*H*-diphosphirene fragment is very similar to that previously observed for the only known free derivative.[3] Interestingly, the boat conformation induces an unusual twist (ca. 42.5°) of the P=C double bond. In most η^1-coordinated complexes the phosphaalkene moiety is nearly planar,[21] whereas twisted P=C bonds have only been reported in sterically congested systems.[22]



Scheme 3. Synthesis of the dinuclear diphosphirene complexes **7** and **8**

Synthesis and Reactivity of Coordinated Diphosphirenylium Salts

Halogenophosphane complexes are very good precursors for coordinated functionalised phosphanes and coordinated

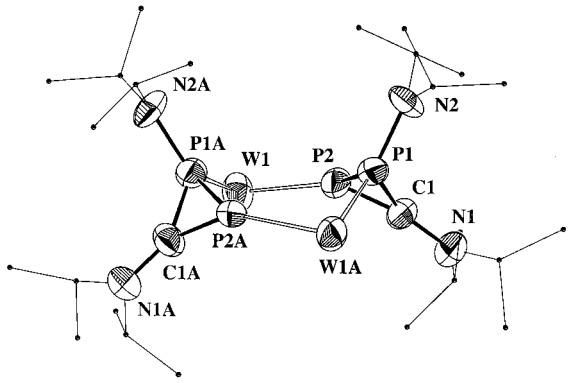
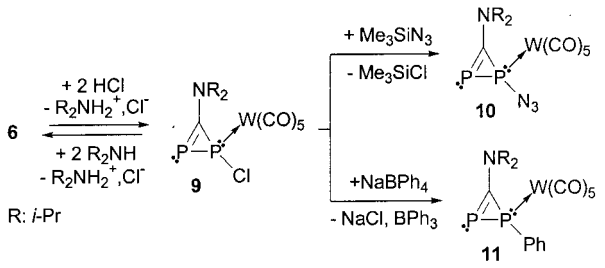


Figure 2. Thermal ellipsoid diagram (30% probability) of **8** showing the atom numbering scheme. All the carbonyl groups have been omitted, and the isopropyl groups have been simplified. Selected bond lengths (Å) and bond angles (°): P1−C1 1.798(15), P1−N2 1.680(11), C1−N1 1.327(18), C1−P2 1.686(15), P1−P2 2.130(5), P2−W1 2.508(3), P1−W1A 2.529(4); P1−C1−N1 138.1(12), P2−C1−N1 146.6(13), P1−C1−P2 75.3(6), C1−P1−P2 49.9(5), C1−P1−N2 113.7(7), P2−P1−N2 113.0(4), C1−P1−W1A 117.4(5), N2−P1−W1A 122.0(5), P2−P1−W1A 120.17(18), C1−P2−P1 54.7(5), C1−P2−W1 150.3(5), P1−P2−W1 143.5(2), P2−W1−P1A 82.6(12).

phosphenium salts, by nucleophilic exchange of the halogen atom and heterolytic cleavage of the P−X bond,[23] respectively. Therefore, *P*-halo-1*H*-diphosphirene complexes seemed to be ideal precursors for coordinated *P*-functionalised-1*H*-diphosphirenes as well as coordinated diphosphirenylium salts. Reaction of **6** with two equivalents of hydrogen chloride[24] in pentane gives the *P*-chloro-1*H*-diphosphirene **9** as a yellow oil in 69% yield (Scheme 4). Although the solubility of **9** in pentane leaves no doubt about the covalent nature of the P−Cl bond, it is interesting to note that the mass spectrum features fragment peaks corresponding to both complexed and uncomplexed diphosphirenylium salts {CI, CH_4, *m/z* = 534 MH^+, 498 $(M - Cl)^+$ and 174 $[M - Cl - W(CO)_5]^+$}.

The chlorine atom of derivative **9** can easily be substituted for an amino substituent, an azido or a phenyl group. Indeed, complex **6** was isolated (85% yield) after treatment of **9** with two equivalents of diisopropylamine in pentane. On addition of a THF solution of azidotrimethylsilane at 45°C, **9** afforded the *P*-azido-1*H*-diphosphirene complex **10** in 40% yield.[25] The replacement of the chlorine atom by an azido group at the λ^3-phosphorus centre was apparent from the mass (CI, $CH_{4,\ m/z}$ = 540), the IR ($\tilde{\nu}_{N3}$ 2130 cm^{-1}) and the ^{31}P NMR spectra [δ = −96.6 (d, J(P,P) = 210 Hz, ^1J(P,W) = 310 Hz, P−N_3), −5.0 (d, J(P,P) = 210 Hz, P=C)]. Finally, treatment of **9** with sodium tetraphenylborate in dichloromethane at room temperature afforded the *P*-phenyl-1*H*-diphosphirene **11** (60% yield) (Scheme 4, Table 2). The formation of **11** probably results from the ionization of the P−Cl bond of **9** leading to a transient diphosphirenylium salt, which abstracts a phenyl group from the tetraphenylborate counterion.[26]

In order to prevent nucleophile transfer, ionization of **9** was carried out in dichloromethane solution at −78°C with either silver trifluoromethanesulfonate,[27] or aluminium or gallium trichloride. The corresponding coordinated diphos-



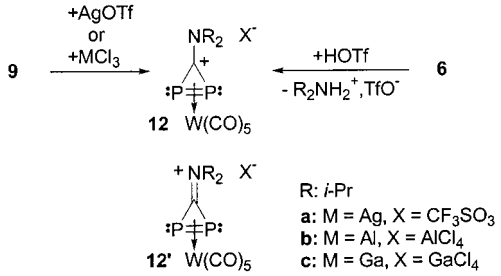
Scheme 4. Synthesis of the *P*-functionalised 1*H*-diphosphirene complexes **9**−**11**

Table 2. Selected spectroscopic data (δ in ppm, *J* in Hz) for the 1*H*-diphosphirene complexes **6**, **9**, **10**, **11**, **13** and **14**.

	6	**9**	**10**	**11**	**13**	**14**
δ(P=C)	+15.0	+34.6	−5.0	−60.0	+33.7	+43.2[a]
δ(σ^4-P)	−123.0	−75.5	−96.6	−177.5	−67.4	−12.1[b]
J(P,P)	164	218	210	148	199	238
^1J(P,W)	295	308	310	257	305	323

[a] *J*(P,F) = 121 Hz. − [b] *J*(P,F) = 1116 Hz.

phirenylium salts **12a**−**c** were isolated as highly air- and moisture-sensitive brown oils in high yields (90−95%). Note that the heterolytic cleavage of the P−N bond of complex **6** with 2 equivalents of trifluoromethanesulfonic acid directly afforded the diphosphirenylium cation **12a** in near quantitative yield (Scheme 5). The structure of derivatives **12a**−**c** and, in particular, the η^2-coordination of the heterocycle (through the P=P bond), has been clearly established by multinuclear NMR and IR spectroscopy, and mass spectrometry.[12] The stability of **12a**−**c** (stable for weeks in solution at room temperature) is almost certainly due to the presence of the metal fragment, but also to the effective π-donation of the nitrogen: **12′** is likely to be the major contributing resonance structure.



Scheme 5. Synthesis of the mononuclear diphosphirenylium salt complexes **12**

Computational Studies

In order to gain more of an insight into the role of the amino substituent and to rationalize the η^2-coordination mode, theoretical calculations were performed on model derivatives **G1**,**2** and **12d**−**g** at the SCF/DZP and B3LYP/DZP levels. The optimized geometric data and atomic charges of derivatives **G1** and **G2** (R = H and NH_2, respectively) are listed in Table 3. Both cations adopt perfectly planar geometries with C_{2v} symmetry. Amino-substitution induces a significant shortening of the P−P bond while the P−C bonds are slightly elongated. The C−N bond length in **G2** is typical for C=N double bonds and comparable with the value found in the tris(dimethylamino)cyclopropenium salt.[28] These data, along with the values of Mulliken and π-charges calculated for **G2**, strongly suggest that the positive charge is shifted outside the ring toward the nitrogen atom. Therefore, the well-established[29] effect of amino substituents on the stability of cyclopropenium salts is also effective for the related diphosphorus-containing species **G**.

It is of further interest to analyse the frontier orbital systems in **G1**,**2**. A detailed listing of the orbitals HOMO-2, HOMO-1, and HOMO is presented in Table 4. It must be noted that as all orbital energies are taken from the results of the energy-optimized RHF calculation of the geometries, orbital energies are meaningful only for the occupied orbitals. In the parent system **G1**, the HOMO and HOMO-1 refer to symmetric and antisymmetric combinations of the two phosphorus lone pairs (a_1 and b_2 orbitals, respectively) while the HOMO-2 corresponds to a π_{PP}-orbital (b_1) which is perpendicular to the ring. The situation is totally different for the amino-substituted cation **G2**. Indeed, the HOMO now refers to the π_{PP}-orbital (b_1) whereas the HOMO-1 and HOMO-2 are almost degenerate and correspond to the a_1 and b_2 orbitals (Figure 3). Thus, the frontier orbital system of **G2** is in agreement with the observed η^2-coordination mode and, in order to complete the theoretical study, the geometry of the isomeric η^1- and η^2-complexes **12d** and **12e** (R = NH_2) were optimized at the B3LYP/DZ(P) level (Figure 4). It is interesting to note that the geometries of the three-membered rings are very similar to those calculated for the free derivative **G2**. The only noticeable difference is the entirely understandable elongation of the P−P bond for the η^1-complex **12d** (**G2** 2.11 Å; **12d** 2.23 Å) and to an even greater extent for the η^2-complex **12e** (2.31 Å). As expected, the η^2-complex **12e** is the more stable isomer, but it is interesting to note that it lies only 16 kJ mol^{-1} below the corresponding η^1-complex **12d**. The influence of the amino group on the coordination mode is shown by the calculations performed for the related complexes **12f,g** featuring the parent cation **G1** as ligand. Indeed, geometry optimization of an η^2-complex of type **12e** results in the η^3-complex **14g**. The tungsten interacts with all the atoms of the three-membered ring of **14g**, as shown by the deviation of the C−H bond from the ring plane (21°) and by the W−P and W−C bond lengths (2.72 and 2.39 Å, respectively, relative to 2.73 and 3.06 Å for **12e**). This η^3-coordination mode results in a reinforced diphosphirenylium salt-metal binding energy (240 kJ mol^{-1} compared to 166 kJ mol^{-1} for **12e**), and thus, the corresponding η^1-complex **12f** is substantially higher in energy (57 kJ mol^{-1}). As far as we are aware, there are no previous examples in which the $W(CO)_5$ fragment is η^3-coordinated.

In the hope of preparing hitherto unknown 3*H*-diphosphirenes **E**, the diphosphirenylium salt complex **12a** was

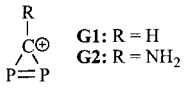


Table 3. Optimized geometry (bond lengths in Å and bond angles in degrees) and atomic charges for derivatives **G1** and **G2**.

	G1 SCF/DZP	**G1** B3LYP/DZP	**G2** SCF/DZP	**G2** B3LYP/DZP
P−P	2.108	2.159	2.059	2.110
P−C	1.706	1.729	1.7051	1.773
C−R	1.075	1.088	1.298	1.312
PCP	76.4	77.3	72.0	73.0
PCR	141.8	141.4	144.0	143.5
q(P)[a]	0.5	0.5	0.38	0.37
q(C)[a]	0	0	0.03	−0.08
q(R)[a]	−	−	0.21	0.34
q(P)[b]	0.38	0.38	0.20	0.2
q(C)[b]	0.24	0.24	0.24	0.15
q(R)[b]	−	−	0.36	0.45

[a] Mulliken charge. − [b] π-charge.

Table 4. Frontier orbital energies (in eV) of cations **G1** and **G2**.

	HOMO-2	HOMO-1	HOMO
G1	−18.4 (b_1)	−17.8 (b_2)	−17.0 (a_1)
G2	−16.7 (b_2)	−16.6 (a_1)	−15.7 (b_1)

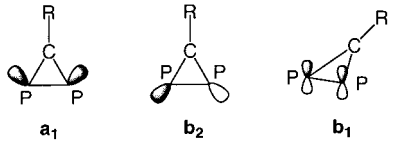


Figure 3. Schematic representation of the molecular orbitals calculated for the model diphosphirenylium salts **G1** and **G2**.

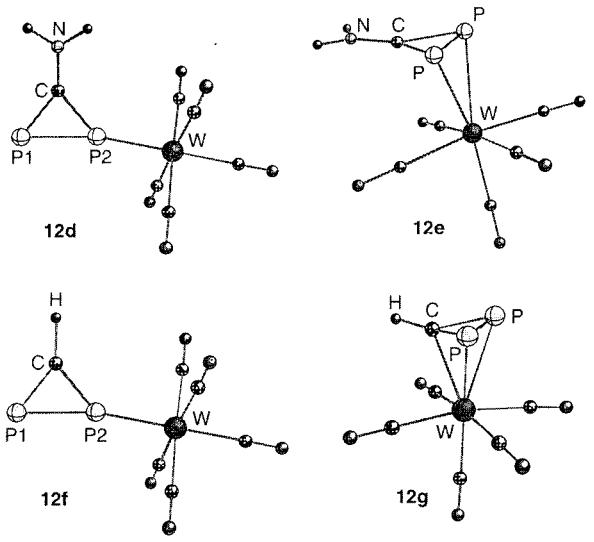
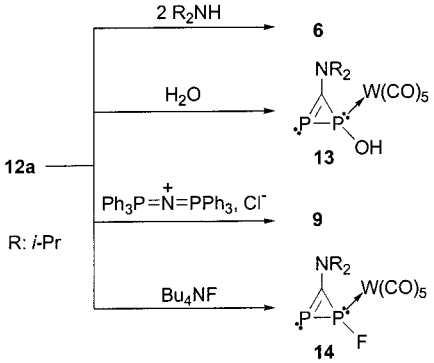


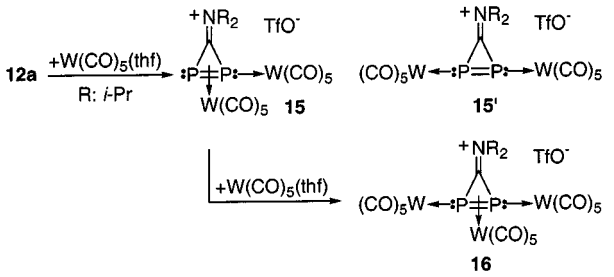
Figure 4. Ball-and-stick views of the calculated structures (at the B3LYP/DZP level) of the η^1-, η^2- and η^3-diphosphirenylium salt complexes **12d−g**. Selected bond lengths (Å): **12d**: N−C 1.33, C−P1 1.78, C−P2 1.77, P2−W 2.40; **12e**: N−C 1.32, C−P1 1.80, P1−P2 2.20, P1−W 2.73; **12f**: H−C 1.09, C−P1 1.73, C−P2 1.75, P2−W 2.37; **12g**: H−C 1.32, C−P 1.79, P−P 2.20, P−W 2.72, C−W 2.39.

then treated with various nucleophiles. However, using diisopropylamine (two equivalents), water, bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) or tetrabutylammonium fluoride, the corresponding 1*H*-diphosphirene complexes **6**, **13**,[30] **9** and **14** were, according to ^{31}P-NMR spectroscopy, formed quantitatively (Scheme 6). In all cases, the presence of the 1*H*-diphosphirene moiety was evidenced by the typical AX spin system observed in the ^{31}P-NMR spectra (Table 2). The presence of the hydroxy or fluoro functionality was deduced from the mass spectrum of **13** (CI, CH_4, m/z = 544), and the ^{31}P and ^{19}F NMR spectra of **14** {^{31}P: δ = −12.1 [dd, J(P,P) = 238 Hz, ^1J(P,W) 323 Hz, J(P,F) = 1116 Hz, P−F], 43.2 [dd, J(P,P) = 238 Hz, J(P,H) = 121 Hz, P=C]; ^{19}F: δ = −14.1 [dd, J(P,F) = 1116 and 121 Hz]}.



Scheme 6. Reaction of the diphosphirenylium salt complex **12a** with various nucleophiles

We then studied the coordination chemistry of the diphosphirenylium salt **12a**, since it can potentially act as a 2-, 4- or 6-electron ligand. The reaction of **12a** with [W(CO)$_5$(thf)] in dichloromethane solution was monitored by ^{31}P NMR spectroscopy. On addition of one equivalent of [W(CO)$_5$(thf)], the sharp singlet corresponding to **12a** (δ = −157.4) disappears to give a broad signal centred at δ = −130. Addition of an excess of [W(CO)$_5$(thf)] subsequently converts the broad signal into a sharp singlet at δ = −74.1.



Scheme 7. Synthesis of the di- and trinuclear diphosphirenylium salt complexes **15** and **16**

This chemical shift, in the range expected for a three-membered phosphorus heterocycle,[32] and the presence of three different *J*(P,W) coupling constants (176, 61 and 45 Hz)[33] strongly support the trinuclear structure **16** (Scheme 7). In addition, the ^{13}C NMR spectrum of **16** reveals the presence of two types of $W(CO)_5$ fragment {δ = 193.6 [t, *J*(P,C) < 1 Hz, ^1J(C,W) = 127 Hz, CO_e], 194.5 (s, CO_a) and 213.6 (s, CO_e), 214.7 (s, CO_a)}. By comparison with those observed for **12a** {δ = 189.3 [t, *J*(P,C) = 4 Hz, ^1J(C,W) = 122 Hz, CO_e], 194.4 [t, *J*(P,C) < 1 Hz, CO_a]}, the signals at δ = 193.6 and 194.5 can be assigned to the η^2-$PW(CO)_5$ moiety while the deshielding of the other two signals (Δδ ≈ 20 ppm) can be classically[34] attributed to the η^1-coordination mode of the corresponding $W(CO)_5$ fragments. Taking into account the trinuclear structure of **16**, the intermediate broad signal detected by ^{31}P NMR spectroscopy is probably due to the dinuclear tungsten complex, for which an equilibrium between the structures **15** and **15′** is likely to occur. Indeed, calculations have clearly shown a small energy difference between η^1- and η^2-coordination modes for the model compounds **12d** and **12e** (see above). The formation of the mono-, di- and trinuclear diphosphirenylium complexes **12**, **15** and **16**, respectively, shows that the coordination chemistry of diphosphirenylium salts **G** shows some resemblance to that of diphosphenes RP=PR.[35]

Conclusion

We have shown that the 1*H*-diphosphirene **3**, which is easily available from the corresponding diphosphirenium salt **1**, can act as a 2- or 4-electron ligand to afford mono- and dinuclear tungsten complexes. Furthermore, not only can this ligand be modified in the coordination sphere of tungsten, but several coordinated diphosphirenylium salts have been prepared and isolated.[36]

These results as a whole clearly demonstrate that diphosphirenylium salts **G** merit further study, and that the synthesis of a noncomplexed derivative remains an exciting challenge. Moreover, the reactivity of these cations has up to now been governed by the electrophilicity of the phosphorus centres, and it would be particularly interesting to attempt to force the system to react at the carbon atom, which should lead to the hitherto unknown 3*H*-diphosphirenes **E**.

Experimental Section

All manipulations were performed under argon with standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AC80, AC200, WM250 or AMX400 spectrometers. Chemical shifts are reported in ppm relative to Me_4Si as external standard (^1H and ^{13}C) or with a positive sign, in ppm, relative to external 85% H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin−Elmer FT-IR Spectrometer 1725 X. Mass spectra were obtained on a Ribermag R10 10E instrument.

***C*-Diisopropylamino-*C*-[bis(diisopropylamino)phosphino]phosphaalkenes (2)**: To a THF solution (5 mL) of the diphosphirenium salt **1** (0.46 g, 1 mmol) was added, at −78°C, 1 equiv. of $LiAlH_4$ (38 mg, 1 mmol). The solution was warmed to room temp., the solvent removed in vacuo, and the residue extracted with pentane (15 mL). After filtration and evaporation of pentane, compound **2** (as a 50:50 mixture of *Z* and *E* isomers) was obtained as a yellow powder (0.30 g, 80%). − M.p. 25−30°C. − ^1H NMR (C_6D_6): δ = 1.20−1.35 (m, 72 H, CH_3), 3.7−4.0 (m, 12 H, CHN), 4.66 (dd, ^1J(P,H) = 174 Hz, ^3J(P,H) = 1.0 Hz, 1 H, P−H, isomer 1), 4.96 (dd, ^1J(P,H) = 138 Hz, ^3J(P,H) = 7.4 Hz, 1 H, P−H, isomer 2). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 205.1 (dd, ^1J(P,C) = 97.6 and 40.1 Hz, PCP), 212.3 (dd, ^1J(P,C) = 65.4 and 58.8 Hz, PCP). − ^{31}P NMR (C_6D_6): δ = 23.8 (dd, ^2J(P,P) = 40 Hz, ^1J(P,H) = 138 Hz, P−H, isomer 1), 34.3 (d, ^1J(P,H) = 174 Hz, P−H, isomer 2), 53.7 (d, ^2J(P,P) = 40 Hz, P−N*i*Pr_2, isomer 1), 55.9 (s, P−N*i*Pr_2, isomer 2). − $C_{19}H_{43}N_3P_2$ (375.3): calcd. C 60.77, H 11.54, N 11.19; found C 60.52, H 11.38, N 11.00.

1,3-Bis(diisopropylamino)-1*H*-diphosphirene (3): To a THF solution (5 mL) of phosphinophosphaalkenes **2** (0.37 g, 1 mmol) was added, at −78°C, a catalytic amount of $BF_3{\cdot}Et_2O$ (14 mg, 0.1 mmol). The solution was warmed to room temp., and stirred for 1 h (the reaction being monitored by ^{31}P NMR spectroscopy). The solvent was then removed in vacuo and the residue extracted with pentane (15 mL). After filtration and evaporation of pentane, compound **3** was obtained as a yellow oil (0.17 g; 62%). − ^1H NMR (C_6D_6): δ 0.95 (d, ^3J(H,H) = 6.6 Hz, 6 H, CH_3), 1.13 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH_3), 1.15 (d, ^3J(H,H) = 6.6 Hz, 6 H, CH_3), 1.32 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH_3), 3.60 (sept, ^3J(H,H) = 6.7 Hz, 2 H, CHN), 4.19 (sept d, ^3J(H,H) = 6.6 Hz, ^3J(P,H) = 1.8 Hz, 2 H, CHN). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 19.1 (d, *J*(P,C) = 4.9 Hz, CH_3), 20.1 (d, *J*(P,C) = 2.7 Hz, CH_3), 21.6 (d, *J*(P,C) = 2.1 Hz, CH_3), 21.8 (s, CH_3), 24.2 (d, *J*(P,C) = 12.2 Hz, CH_3), 24.5 (d, *J*(P,C) = 5.2 Hz, CH_3), 43.4 (d, *J*(P,C) = 5.6 Hz, CHN), 51.3 (s, CHN), 58.4 (t_{like}, *J*(P,C) = 4.2 Hz, CHN), 191.2 (dd, *J*(P,C) = 82.2 and 77.9 Hz, PCP). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −121.7 (d, *J*(P,P) = 121 Hz, P−N*i*Pr_2), −23.7 (*J*(P,P) = 121 Hz, σ^2-P). − MS (NH_3, CI); *m*/*z*: 275 (MH^+). − $C_{13}H_{28}N_2P_2$ (274.2): calcd C 56.92, H 10.29, N 10.21; found C 57.04, H 10.43, N 9.87.

[1,1,3-Tris(diisopropylamino)diphosphirenium Salt][$W(CO)_5$] (4): To a THF solution (30 mL) of the diphosphirenium salt **1** (0.46 g, 1 mmol) was added, at −78°C, an excess of [$W(CO)_5$(thf)] (10 mL, 0.3 M solution in THF, 3 mmol). The solution was warmed to room temp. and stirred for 1 h at room temp. Complex **4** was characterized in solution without further purification. − ^{31}P NMR (THF): δ = −33.9 (d quint, *J*(P,P) = 130 Hz, ^3J(P,H) = 20 Hz, P−N*i*Pr_2), 39.9 (d, *J*(P,P) = 130 Hz, ^1J(P,W) = 249 Hz, P=C).

{*C*-Diisopropylamino-*C*-[bis(diisopropylamino)phosphino]phosphaalkene}[$W(CO)_5$] (5): To a THF solution (5 mL) of phosphinophosphaalkenes **2** (0.37 g, 1 mmol) was added, at −78°C, 1 equiv. of [$W(CO)_5$(thf)] (5 mL, 0.2 M solution in THF, 1 mmol). The solu-

tion was warmed to 0°C, the solvent removed in vacuo, the residue redissolved in deuterated toluene and complex **5** characterized in solution at 0°C. – ^{1}H NMR (C_7D_8): δ = 1.10–1.60 (m, 36 H, CH_3), 3.30–4.20 (m, 6 H, CHN), 4.95 (d, 1 H, ^1J(P,H) = 267 Hz, P–H); ^{13}C{^{1}H} NMR (C_7D_8): δ = 20.0–25.0 (m, CH_3), 50.2 (s, CHN), 55.7 (d, J(P,C) = 45.9 Hz, CHN), 58.7 (d, J(P,C) = 29.7 Hz, CHN), 199.9 (s, ^1J(C,W) = 126.1 Hz, CO_e), 203.3 (d, ^2J(P,C) = 7.7 Hz, CO_a), 233.3 (dd, ^1J(P,C) = 72.3 and 50.3 Hz, PCP). – ^{31}P NMR (C_7D_8): δ = –71.0 (d, ^1J(P,H) = 267 Hz, ^1J(P,W) = 129 Hz, P–H), 66.5 (s, P–N*i*Pr$_2$). – Complex **5** was also obtained by adding an excess of lithium aluminium hydride to a THF solution of the diphosphirenium salt complex **4** at –78°C.

[1,3-Bis(diisopropylamino)-1*H*-diphosphirene][W(CO)$_5$] (6): To a THF solution (5 mL) of 1*H*-diphosphirene **3** (0.27 g, 1 mmol) was added, at –78°C, 1 equiv. of [W(CO)$_5$(thf)] (5 mL, 0.2 M solution in THF, 1 mmol). The solution was warmed to room temp., the solvent removed in vacuo and the residue extracted with pentane (15 mL). After filtration and evaporation of pentane, complex **6** was obtained as a yellow oil (0.39 g; 65%). – ^{1}H NMR (C_6D_6): δ = 1.18 (d, ^3J(H,H) = 6.9 Hz, 6 H, CH_3), 1.25 (d, ^3J(H,H) = 6.9 Hz, 6 H, CH_3), 1.29 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 1.37 (d, ^3J(H,H) = 6.6 Hz, 3 H, CH_3), 1.39 (d, ^3J(H,H) = 6.6 Hz, 3 H, CH_3), 1.51 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 3.63 (sept d, ^3J(H,H) = 6.9 Hz, ^3J(P,H) = 13.8 Hz, 2 H, CHNP), 3.97 (sept, ^3J(H,H) = 6.6 Hz, 1 H, CHN), 4.51 (sept, ^3J(H,H) = 6.7 Hz, 1 H, CHN). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 18.3 (d, J(P,C) = 5.6 Hz, CH_3), 19.0 (d, J(P,C) = 3.5 Hz, CH_3), 20.7 (s, CH_3), 23.8 (s, CH_3), 48.8 (s, CHN), 49.2 (d, J(P,C) = 7.7 Hz, CHNP), 62.4 (dd, J(P,C) = 5.8 and 3.8 Hz, CHN), 195.9 (dd, J(P,C) = 80.6 and 48.4 Hz, PCP), 197.6 (d, ^2J(P,C) = 8.7 Hz, ^1J(C,W) = 126.9 Hz, CO_e), 200.2 (d, ^2J(P,C) = 33.1 Hz, ^1J(C,W) = 149.9 Hz, CO_a). – ^{31}P{^{1}H} NMR (C_6D_6): δ = –123.0 (d, J(P,P) = 164 Hz, ^1J(P,W) = 295 Hz, P–N*i*Pr$_2$), 15.0 (J(P,P) = 164 Hz, σ^2-P). – IR (THF): $\tilde{\nu}$ = 1930 (vs), 1938 (vs) and 2069 (s) cm^{-1} (CO). – $C_{18}H_{28}N_2O_5P_2W$ (598.1): calcd C 36.14, H 4.72, N 4.68; found C 36.35, H 4.53, N 4.62.

[1,3-Bis(diisopropylamino)-1*H*-diphosphirene][W(CO)$_5$]$_2$ (7): To a THF solution (5 mL) of 1*H*-diphosphirene **3** (0.27 g, 1 mmol) was added, at –78°C, 2 equiv. of [W(CO)$_5$(thf)] (5 mL, 0.4 M solution in THF, 2 mmol). The solution was warmed to room temp., the solvent removed in vacuo and the residue extracted with pentane (15 mL). After filtration, complex **7** crystallized from the pentane solution as a yellow, microcrystalline powder (0.85 g; 92%). – M.p. 128–129°C (dec). – ^{1}H NMR (C_6D_6): δ = 0.86 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 1.08 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 1.10 (d, ^3J(H,H) = 6.9 Hz, 6 H, CH_3), 1.19 (d, ^3J(H,H) = 6.9 Hz, 6 H, CH_3), 1.21 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3), 1.32 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3), 3.39 (sept, ^3J(H,H) = 6.8 Hz, 1 H, CHN), 3.66 (sept d, ^3J(H,H) = 6.9 Hz, ^3J(P,H) = 15.5 Hz, 2 H, CHNP), 4.27 (sept, ^3J(H,H) = 6.7 Hz, 1 H, CHN). – ^{13}C{^{1}H} NMR (C_6D_6): δ 20.0 (d, J(P,C) = 3.2 Hz, CH_3), 20.3 (d, J(P,C) = 2.1 Hz, CH_3), 20.4 (d, J(P,C) = 2.5 Hz, CH_3), 20.9 (d, J(P,C) = 2.1 Hz, CH_3), 24.4 (s, CH_3), 24.6 (d, J(P,C) = 3.1 Hz, CH_3), 49.7 (d, J(P,C) = 1.7 Hz, CHN), 50.4 (d, J(P,C) = 9.0 Hz, CHN), 61.5 (d, J(P,C) = 8.0 Hz, CHN), 188.3 (dd, J(P,C) = 46.4 and 37.5 Hz, PCP), 195.7 (d, ^2J(P,C) = 6.2 Hz, ^1J(C,W) = 126.4 Hz, CO_e), 197.6 (dd, J(P,C) = 7.8 and 1.7 Hz, ^1J(C,W) = 127.0 Hz, CO_e), 199.4 (d, ^2J(P,C) = 34.9 Hz, CO_a), 199.7 (d, ^2J(P,C) = 35.2 Hz, CO_a). – ^{31}P{^{1}H} NMR (C_6D_6): δ = –86.9 (d, J(P,P) = 111 Hz, ^1J(P,W) = 296 Hz, P–N*i*Pr$_2$), –6.3 (J(P,P) = 111 Hz, ^1J(P,W) = 209 Hz, P=C). – IR (THF): $\tilde{\nu}$ = 1934 (vs), 1972 (vs), 2067 (s) and 2079 (s) cm^{-1} (CO). – $C_{23}H_{28}N_2O_{10}P_2W_2$ (922.0): calcd C 29.96, H 3.06, N 3.04; found C 30.12, H 2.88, N 2.92.

{[1,3-Bis(diisopropylamino)-1*H*-diphosphirene][W(CO)$_4$]}$_2$ (8): To a THF solution (5 mL) of 1*H*-diphosphirene **3** (0.27 g, 1 mmol) was added, at –78°C, 1 equiv. of [W(CO)$_4$(thf)$_2$] (2.5 mL, 0.4 M solution in THF, 1 mmol). The solution was warmed to room temp., the solvent removed in vacuo and the residue extracted with pentane (15 mL). After filtration, complex **8** crystallized from a pentane/dichloromethane solution at –20°C as yellow crystals (0.26 g; 60%). – M.p. 166–167°C (dec). – ^{1}H NMR (C_6D_6): δ = 1.24 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH_3), 1.33 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH_3), 1.35 (d, ^3J(H,H) = 6.7 Hz, 12 H, CH_3), 1.37 (d, ^3J(H,H) = 6.7 Hz, 12 H, CH_3), 1.39 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH_3), 1.45 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH_3), 3.40 (m, 2 H, CHN), 3.86 (m, 2 H, CHN), 4.04 (sept, ^3J(H,H) = 6.7 Hz, 2 H, CHN), 4.42 (sept, ^3J(H,H) = 6.7 Hz, 2 H, CHN). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 19.3 (s, CH_3), 19.7 (s, CH_3), 20.6 (s, CH_3), 20.8 (s, CH_3), 23.8 (s, CH_3), 24.4 (s, CH_3), 47.8 (s, CHN), 50.1 (s, CHN), 61.7 (d, J(P,C) = 5.7 Hz, CHN), 194.3 (dd, J(P,C) = 52.6 and 37.7 Hz, PCP), 198.2 (s, ^1J(C,W) 129.3 Hz, CO_a), 201.0 (d, ^2J(P,C) = 6.7 Hz, ^1J(C,W) = 130.6 Hz, CO_a), 204.2 (d, ^2J(P,C) = 35.6 Hz, ^1J(C,W) = 158.2 Hz, CO_e), 207.3 (dd, J(P,C) = 37.3 and 6.5 Hz, CO_e). – ^{31}P{^{1}H} NMR (C_6D_6): A_2B_2 system δ –129.4 (P–N*i*Pr$_2$), –28.6 (P=C). – $C_{34}H_{56}N_4O_8P_4W_2$ (1140.2): calcd C 35.81, H 4.95, N 4.91; found C 36.05, H 4.80, N 4.82.

[1-Chloro-3-diisopropylamino-1*H*-diphosphirene][W(CO)$_5$] (9): To an ether solution (6 mL) of complex **6** (0.12 g, 0.2 mmol) was added, at –78°C, 400 μL of a 1 M Et_2O solution of HCl (2 equiv). The solution was warmed to room temp., the solvent removed in vacuo and the residue extracted with pentane (20 mL). After filtration and evaporation of pentane, complex **9** was obtained as a yellow oil (0.07 g; 69%). – ^{1}H NMR (C_6D_6): δ 0.86 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 1.03 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 1.04 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 1.12 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 3.27 (sept, ^3J(H,H) = 6.7 Hz, 1 H, CHN), 4.71 (sept, ^3J(H,H) = 6.7 Hz, 1 H, CHN). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 19.3 (d, J(P,C) = 4.2 Hz, CH_3), 19.5 (d, J(P,C) = 4.6 Hz, CH_3), 20.4 (s, CH_3), 20.5 (s, CH_3), 50.2 (d, J(P,C) = 3.3 Hz, CHN), 63.4 (dd, J(P,C) = 7.3 and 4.8 Hz, CHN), 189.0 (dd, J(P,C) = 88.6 and 34.7 Hz, PCP), 196.7 (d, ^2J(P,C) = 8.6 Hz, ^1J(C,W) = 127.1 Hz, CO_e), 199.5 (d, ^2J(P,C) = 46.8 Hz, CO_a). – ^{31}P{^{1}H} NMR (C_6D_6): δ = –78.5 (d, J(P,P) = 218 Hz, ^1J(P,W) = 308 Hz, P–Cl), 34.6 (d, J(P,P) = 218 Hz, σ^2-P). – IR (pentane): $\tilde{\nu}$ = 1949 (vs), 1959 (vs) and 2079 (s) cm^{-1} (CO). – MS (CH_4, CI); *m*/*z*: 534 (MH^+), 498 [(M–Cl)$^+$], 442 [(M–Cl-*i*Pr)$^+$], 174 {[M–Cl-W(CO)$_5$]$^+$}. – $C_{12}H_{14}ClNO_5P_2W$ (532.9): calcd C 27.02, H 2.65, N 2.63; found C 26.75, H 2.50, N 2.42.

Reaction of complex 9 with *i*Pr$_2$NH: To a THF solution (5 mL) of complex **9** (0.36 g, 0.7 mmol) was added, at room temp., 2 equiv. of diisopropylamine (0.14 g, 1.4 mmol). The solution was warmed to room temp., the solvent removed in vacuo and the residue extracted with pentane (15 mL). After filtration and evaporation of pentane, complex **6** was obtained as a yellow oil (0.40 g; 95%).

[1-Azido-3-diisopropylamino-1*H*-diphosphirene][W(CO)$_5$] (10): To a THF solution (5 mL) of complex **9** (0.36 g, 0.7 mmol) was added, at room temp., 1 equiv. of Me_3SiN_3 (0.08 g, 0.7 mmol). The solution was warmed to 45°C and stirred for 1 h (the reaction was monitored by ^{31}P NMR spectroscopy). The solvent was then removed in vacuo and the residue extracted with pentane (20 mL). After filtration and evaporation of pentane, complex **10** was obtained as a brown oil (0.15 g; 40%). – ^{1}H NMR (C_6D_6): δ = 0.86 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3), 1.02 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3), 1.06 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3), 1.12 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3), 3.30 (sept, ^3J(H,H) = 6.8 Hz, 1 H, CHN), 4.71

(sept, ^3J(H,H) = 6.8 Hz, 1 H, CHN). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 19.1 (d, J(P,C) = 4.5 Hz, CH_3), 19.5 (d, J(P,C) = 4.2 Hz, CH_3), 20.4 (s, CH_3), 20.7 (s, CH_3), 51.3 (d, J(P,C) = 3.3 Hz, CHN), 62.5 (dd, J(P,C) = 36.4 and 4.3 Hz, CHN), 196.4 (d, ^2J(P,C) = 8.8 Hz, ^1J(C,W) = 109.3 Hz, CO_e), 199.0 (d, ^2J(P,C) = 41.9 Hz, CO_a), PCP was not observed. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −96.6 (d, J(P,P) = 210 Hz, ^1J(P,W) = 310 Hz, P−N_3), −5.0 (d, J(P,P) = 210 Hz, σ²-P). − IR (THF): $\tilde{\nu}$ = 2130 (vs) cm^{-1} (NN). − MS (CH_4, CI) *m/z*; 540 (MH^+), 498 [(M-N_3)$^+$]. − $C_{12}H_{14}N_4O_5P_2W$ (540.0): calcd C 26.69, H 2.61, N 10.37; found C 26.83, H 2.74, N 10.23.

[1-Phenyl-3-diisopropylamino-1*H*-diphosphirene][W(CO)$_5$] (11): To a CH_2Cl_2 solution (2 mL) of complex **9** (0.07 g, 0.14 mmol) was added, at −78°C, a CH_2Cl_2 solution (2 mL) of 1 equiv. of $NaBPh_4$ (0.05 g, 0.14 mmol). The solution was warmed to room temp., the solvent removed in vacuo and the residue extracted with pentane (15 mL). After filtration and evaporation of pentane, complex **11** was obtained as a yellow oil (0.05 g; 60%). − ^1H NMR (C_6D_6): δ 0.82 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 1.30 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 1.38 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 1.47 (d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3), 3.88 (sept d, ^3J(H,H) = 6.7 Hz, J(P,H) = 2.1 Hz, 1 H, CHN), 4.28 (sept, ^3J(H,H) = 6.7 Hz, 1 H, CHN), 6.9−7.1 (m, 3 H, $H_{m,p}$), 7.65 (ddd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.5 Hz, J(P,H) = 13.2 Hz, 2 H, H_o). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 19.0 (d, J(P,C) = 3.2 Hz, CH_3), 19.2 (d, J(P,C) = 4.0 Hz, CH_3), 20.2 (s, CH_3), 20.3 (s, CH_3), 49.4 (d, J(P,C) = 3.2 Hz, CHN), 63.2 (dd, J(P,C) = 7.3 and 4.3 Hz, CHN), 129.0 (d, J(P,C) = 10.2 Hz, C_{arom}), 130.5 (d, J(P,C) = 2.0 Hz, C_{arom}), 132.5 (d, J(P,C) = 15.8 Hz, C_{arom}), 197.7 (d, ^2J(P,C) = 8.0 Hz, ^1J(C,W) = 126.3 Hz, CO_e), 199.1 (d, ^2J(P,C) = 30.4 Hz, CO_a), C_i and PCP were not observed. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −177.5 (d, J(P,P) = 148 Hz, ^1J(P,W) = 257 Hz, P−Ph), −60.0 (d, J(P,P) = 148 Hz, σ²-P). − IR (THF): $\tilde{\nu}$ = 1935 (vs), 1943 (vs) et 2071 (s) cm^{-1} (CO). − MS (NH_3, CI) *m/z*; 576 (MH^+), 498 [(M−Ph)$^+$].

[η^2-(3-Diisopropylaminodiphosphirenylium Salt)][W(CO)$_5$] (12): To a CH_2Cl_2 solution (3 mL) of complex **9** (0.15 g, 0.28 mmol) was added, at −78°C, 1 equiv. of $AgCF_3SO_3$ (0.07 g, 0.28 mmol). The solution was warmed to room temp., and silver salts were removed by filtration. Evaporation of CH_2Cl_2 gave the complex **12a** as a yellow oil (0.16 g; 90%). − ^1H NMR ($CDCl_3$): δ = 1.39 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH_3), 1.44 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH_3), 4.34 (sept, ^3J(H,H) = 6.7 Hz, 2 H, CHN). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.2 (s, CH_3), 20.9 (s, CH_3), 63.2 (s, CHN), 119.7 (q, ^1J(C,F) = 319 Hz, CF_3), 189.3 (t, ^2J(P,C) = 4.3 Hz, ^1J(C,W) = 121.5 Hz, CO_e), 194.4 (t, ^2J(P,C) < 1 Hz, CO_a), 205.1 (t, ^1J(P,C) = 90.9 Hz, PCP). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −157.4. − IR (CH_2Cl_2): $\tilde{\nu}$ = 1950 (vs) and 2055 (s) cm^{-1} (CO). − MS (CH_4, CI) *m/z*; 498 (M^+), 470 [(M−CO)$^+$], 442 {[M-2(CO)]$^+$}. − The same salt **12a** was obtained in near quantitative yield (95%) by adding, at −78°C, 2 equivalents of CF_3SO_3H to a CH_2Cl_2 solution of complex **6**. Starting from complex **9** and using $AlCl_3$ or $GaCl_3$ as Lewis acids, complexes **12b** and **12c** could also be obtained in 90% yield. − $C_{12}H_{14}Cl_4GaNO_5P_2W$ (707.6): calcd C 20.31, H 1.99, N 1.97; found C 19.60, H 2.39, N 2.10.

Reactivity of Complex 12a:

− *i*Pr_2NH: To a CH_2Cl_2 solution (4 mL) of complex **14a** (0.14 g, 0.22 mmol) was added, at −78°C, 2 equiv. of *i*Pr_2NH (0.04 g, 0.44 mmol). The solution was warmed to room temp., the solvent removed in vacuo and the residue extracted with pentane (15 mL). After filtration and evaporation of pentane, complex **6** was obtained as a yellow oil (0.12 g; 95%).

− H_2O: A CH_2Cl_2 solution (4 mL) of complex **12a** (0.08 g, 0.13 mmol) was stirred in contact with air for 1 h. Compound **13** (obtained in quantitative yield according to ^{31}P NMR spectroscopy) was analyzed without further purification. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −67.4 (d, J(P,P) = 199 Hz, ^1J(P,W) = 305 Hz, P−OH), 33.7 (d, J(P,P) = 199 Hz, σ²-P). − MS (CH_4, CI); *m/z*: 544 (M+29), 516 (M+1), 498 [(M−OH)$^+$].

− $Ph_3P{=}N{=}PPh_3^+$,Cl^-: To a CH_2Cl_2 solution (4 mL) of complex **12a** (0.14 g, 0.22 mmol) was added, at −78°C, 1 equiv. of $Ph_3P{=}N{=}PPh_3^+$.Cl^- (0.13 g, 0.22 mmol). The solution was warmed to room temp., the solvent removed in vacuo and the residue extracted with pentane (15 mL). After filtration and evaporation of pentane, complex **9** was obtained as a yellow oil (0.11 g; 94%).

− Bu_4NF: To a CH_2Cl_2 solution (4 mL) of complex **12a** (0.14 g, 0.22 mmol) was added, at −78°C, 1 equiv. of Bu_4NF (0.06 g, 0.22 mmol). The solution was warmed to room temp. and compound **14** (obtained in quantitative yield according to ^{31}P NMR spectroscopy) was analyzed without further purification. − ^{19}F NMR (C_6D_6): δ = −14.1 (dd, ^1J(P,F) = 1116 Hz, ^2J(P,F) = 121 Hz) − $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ = −12.1 (dd, J(P,P) = 238 Hz, ^1J(P,F) = 1116 Hz, ^1J(P,W) = 323 Hz, P−F), 43.2 (dd, J(P,P) = 238 Hz, ^2J(P,F) = 121 Hz, σ²-P).

[η^2-(3-Diisopropylaminodiphosphirenylium Salt)][W(CO)$_5$]$_2$ (15): To a $C_2H_4Cl_2$ solution (4 mL) of complex **12a** (0.19 g, 0.3 mmol) was added, at −78°C, 1 equiv. of [W(CO)$_5$(thf)] (3 mL, 0.1 M solution in THF, 0.3 mmol). The solution was warmed to room temp., stirred for 1 h, and compound **15** was analyzed without further purification. − $^{31}P\{^1H\}$ NMR ($C_2H_4Cl_2$): δ = −130 (broad).

[η^2-(3-Diisopropylaminodiphosphirenylium Salt)][W(CO)$_5$]$_3$ (16): To a CD_2Cl_2 solution (4 mL) of complex **12a** (0.19 g, 0.3 mmol) was added, at −78°C, 2 equiv. of [W(CO)$_5$(thf)] (6 mL, 0.1 M solution in THF, 0.6 mmol). The solution was warmed to room temp., stirred for 1 h, the solvent removed in vacuo, and the compound **16** (obtained in quantitative yield according to ^{31}P NMR spectroscopy) was analyzed without any further purification. − ^1H NMR (CD_2Cl_2): δ = 1.60 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH_3), 1.63 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH_3), 4.48 (sept, ^3J(H,H) = 6.8 Hz, 2 H, CHN). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 20.1 (s, CH_3), 21.3 (s, CH_3), 59.3 (s, CHN), 118.5 (q, ^1J(C,F) = 318 Hz, CF_3), 193.6 (t, J(P,C) < 1 Hz, ^1J(C,W) = 127.1 Hz, CO_e), 194.5 (s, CO_a), 213.6 (s, CO_a), 214.7 (s, CO_e), PCP was not observed. − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −74.1 (J(P,W) = 176, 61 and 45 Hz).

X-Ray Crystal Structure Determination of 2 and 8: Crystal data for all structures are presented in Table 1. Data for **2** and **8** were collected at low temperatures using an oil-coated, shock-cooled crystal[37] on a Stoe-IPDS with Mo-*Kα* (λ = 0.71073 Å) radiation. The structures were solved by direct methods using SHELXS-97[38] and refined with all data on F^2 using SHELXL-97.[39] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. A numerical absorption correction was employed for structure **8**,[40] the min./max. transmissions are 0.4325/0.568. Refinement of an inversion twin parameter[41] [x = 0.49(2), where × = 0 for the correct absolute structure and +1 for the inverted structure] confirmed a racemic twinning of **8**. The two positions for the disordered hydrogen atoms in **2** were localized by Fourier synthesis and refined by using distance restraints. In **8** two half molecules of CH_2Cl_2 located on the twofold axis are refined anisotropically. 80 ADP and distance restraints were used for the refinement of **8**.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cam-

bridge Crystallographic Data Centre as supplementary publications nos. CCDC-121633 (2) and −121634 (8). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336−033; E-mail: deposit@ccdc.cam.ac.uk].

Computational details. We have used standard, well-calibrated computational methods incorporated into the Gaussian 92 program.[42] In view of the size of the molecules concerned, typical approximations were made so that the computations were actually performed on model compounds, in which the diisopropylamino substituent was replaced by an hydrogen atom, or an amino group. Geometries were optimized with the complete DZP basis set[43] at both SCF and B3LYP[44] levels. For the free species, vibrational frequencies were calculated for the various stationary points located, to check that these are true minima. Pseudo-potentials were adopted for W[45] and P[46] atoms in calculations on complexes **12d−g**; the use of these pseudopotentials was shown to lead to trivial differences relative to all-electron results for the ligands G1,2. Geometries for **12d−g** were fully optimized under C_s symmetry at the B3LYP level, employing a basis with polarisation functions on P atoms only. Final binding energies (B3LYP) were obtained with a basis containing polarisation functions on all atoms (f-type exponent 0.5 for W).

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