4,4-*p*-Biphenyl bis-phosphinidene: generation of a bis-W(CO)$_5$ complex and *ab initio* calculation of its electronic structure

Ngoc Hoa Tran-Huy,*[a] Hung Thanh Le,[b,c] Francois Mathey[a] and Minh Tho Nguyen*[b]

[a] *Laboratoire Hétéroéléments et Coordination, URA 7653 CNRS, DCPH, Ecole Polytechnique, F-91128 Palaiseau Cédex, France. E-mail: hoa.tranhuy@polytechnique.fr*
[b] *Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium. E-mail: minh.nguyen@chem.kuleuven.ac.be*
[c] *Group of Computational Chemistry, Faculty of Chemical Engineering, Ho Chi Minh City University of Technology, Vietnam*

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The (bis-7-phosphanorbornadiene-7-yl)-biphenyl was prepared from the reaction of the 4,4′-biphenyl dianion with the readily available 1-cyano-3,4-dimethylphosphole. The resulting complex was then used as a precursor of the 4,4′-*p*-biphenyl bisphosphinidene (P–C_6H_4–C_6H_4–P), which is trapped either by insertion reaction with MeOH leading to the bisphosphine complex or by [1+2] cycloaddition with diphenylacetylene, leading to the 4,4′-*p*-biphenyl bisphosphirene complex. *Ab initio* calculations on biphosphinidene were carried out using the CASSCF/CASPT2 method in conjunction with the 6-31G(d) basis set and both (12 electron–12 orbital) and (14 electron–14 orbital) active spaces that include all four lone pair orbitals of phosphorus atoms and the higher-lying phenyl p-orbitals. The calculated results pointed out that, in the ligand-free form, the parent 4,4′-*p*-biphenyl bis-phosphinidene (BPBP) exhibits a quintet ground electronic state (^{5}A) having a twisted geometry, but with small quintet-singlet and quintet-triplet ($^5A < {}^1A_g < {}^3B_{1u}$) energy gaps of only 6 and 16 kJ mol^{-1}, respectively. While the singlet and triplet states need to be treated by multi-reference wavefunctions, the lowest-lying quintet state ^{5}A can essentially be described by HF-based single reference methods. In this high-spin state, BPBP is formed by a loose connection between two phenyl phosphinidenes in keeping the spin state of the P-atoms intact, leading to a weak coupling between phosphorus non-bonding electrons through the biphenyl moiety.

Introduction

Transient terminal electrophilic phosphinidenes stabilized by complexation with transition metals [RP ⟶ M] with M= Cr(CO)$_5$, Mo(CO)$_5$, W(CO)$_5$, have proved to be powerful building blocks in the synthesis of organophosphorus compounds. Their versatile carbene-like chemistry is currently under active investigation.[1,2]

Their usual precursors, the corresponding 7-phosphanorbornadiene derivatives, could be obtained on a large scale, starting from 3,4-dimethylphosphole derivatives.[3] Furthermore, some decomplexation techniques have already been available[4–6] as well as the possibility to vary the substituents on the phosphorus atom.[7–9] This turns out to be quite promising for access to different novel classes of organophosphorus molecules in which a large range of substituents on the phosphorus could be incorporated.

In the same vein, some effort has been devoted toward the preparation of precursors giving rise to bis-phosphinidenes that exhibit two distinct phosphinidene functions in the same molecule. Nevertheless, as far as we are aware, there have been only two earlier reports by our group on these materials. The first synthesis, in 1987, of bis-phosphinidene complexes in which both phosphinidene moieties are separated from each other by an alkyl chain, brought some nice P,P′–W(CO)$_4$ chelate complexes.[10] The more recently reported complex having a *cis*-but-2-ene chain between two phosphorus atoms afforded new diphosphorus bicycles following intramolecular processes.[11] In view of such scarcity of information on this class of interesting compounds, we have attempted to prepare a new precursor for bisphosphinidene complexes where both phosphinidene units are situated in a *para* position on a biphenyl system. An obvious interest is that in such system, they could be connected to each other by a π-conjugated framework. The use of a phenyl ring or biphenyl moiety as the linking unit in biscarbenes and bisnitrenes has also actively been investigated by means of both experimental and theoretical methods.[12] Some of these derivatives exhibit an inherent biradical or biradical-like electronic character and are involved in various photochemical and thermal processes of organic compounds. From a practical point of view, these organic materials have interesting magnetic properties and as such could be considered as promising building blocks for organic magnets.[13] From a theoretical aspect, they are obvious targets to gain some insights into the through space electron spin interactions.[14,15]

The purpose of this work is twofold: first, we carried out the actual synthesis of a precursor for the 4,4-*p*-biphenyl bisphosphinidene complex (referred to hereafter as BPBP), namely the [4,4-bis-(2,3-bis-methoxycarbonyl-5,6-dimethyl-7-phosphanorbornadien-7-yl)-biphenyl]decacarbonylditungsten. The characteristic reactions of the transient bisphosphinidene complexes with some trapping reagents such as methanol or diphenyl acetylene are also here reported. Second, we determined the electronic structure of the complex-free BPBP in optimizing the geometric parameters of its different electronic states making use of *ab initio* molecular orbital calculations with the aim to identify its ground electronic state. It is well known that in the coordination sphere of a metal fragment, the complex has a singlet closed-shell state.

Results and discussion

Synthesis of a precursor and trapping reactions

Let us first describe the synthesis of the 4,4′-bis-(3,4-dimethylphospholyl) biphenyl **2** by the reaction of the 4,4′-biphenyl

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dianion[16] with the 1-cyano-3,4-dimethylphosphole **1** performed in THF at low temperature −40 °C which resulted in 50% yield. The product **2** was subsequently complexed with pentacarbonyl tungsten by means of $CH_3CNW(CO)_5$ at 55 °C for one hour and then converted to the appropriate 7-phosphanorbornadiene precursor **4** by reaction with dimethyl acetylenedicarboxylate (*cf.* eqn. (1)).

The cycloaddition takes place on the phosphole side opposite to the tungsten complexing group as shown by the couplings of Me–C_5, Me–C_6, MeO_2C–C_2, MeO_2C–C_3 with phosphorus: $\delta(C_5,C_6)$: 140.67, $^2J(C\text{–}P)$ = 13.9 Hz; $\delta(C_2,C_3)$: 145.81 and $^2J(C\text{–}P)$ = 4.2 Hz. The $^2J(C\text{–}P)$ are highly dependent on the C–C–P–W dihedral angles and these data correspond closely to those of the structurally characterized 7-phosphanorbornadiene complexes.[3]

Two trapping experiments of the transient bis-phosphinidene complex with MeOH and diphenylacetylene gave satisfactory results as illustrated in eqn. (2).

The complex **4** reacted with an excess of MeOH, in the presence of CuCl in catalytic amount, gave rise to the bismethoxyphosphine **5** in 72% yield. The reaction of **4** with diphenylacetylene at 55 °C, in the presence of CuCl as catalyst, yielded the bis-phosphirene complex **6** in 60% yield. This latter can be also directly prepared from the bis-phosphole complex **3** by heating at 110 °C, with an excess of dimethylacetylenedicarboxylate and diphenylacetylene, for 48 h. In ^{31}P NMR, the complex **6** appeared at high field with the characteristics of −161.87 ppm (toluene) and $^1J(P\text{–}W)$ = 268.56 Hz.

Molecular orbital calculations

In this section, we complement the experimental results by quantum chemical computations. The purpose was an attempt to determine the electronic ground state of the free BPBP unit ($P\text{–}C_6H_4\text{–}C_6H_4\text{–}P$), without the presence of any metal ligand. All *ab initio* molecular orbital calculations were carried out using the MOLCAS[17] set of programs.

As in the analogous carbenes (R–C–R′) and nitrenes (R–N), the two non-bonding electrons centered at the monocoordinated phosphorus atom of a phosphinidene (R–P) could be distributed into two different orbitals. Such a 2 electron–2 orbital system usually leads to competition between a triplet, an open-shell singlet and a closed-shell singlet state. In phosphinidenes, the triplet manifold usually gives rise to the dominant lower-lying electronic state in which the substituents R plays a smaller effect:

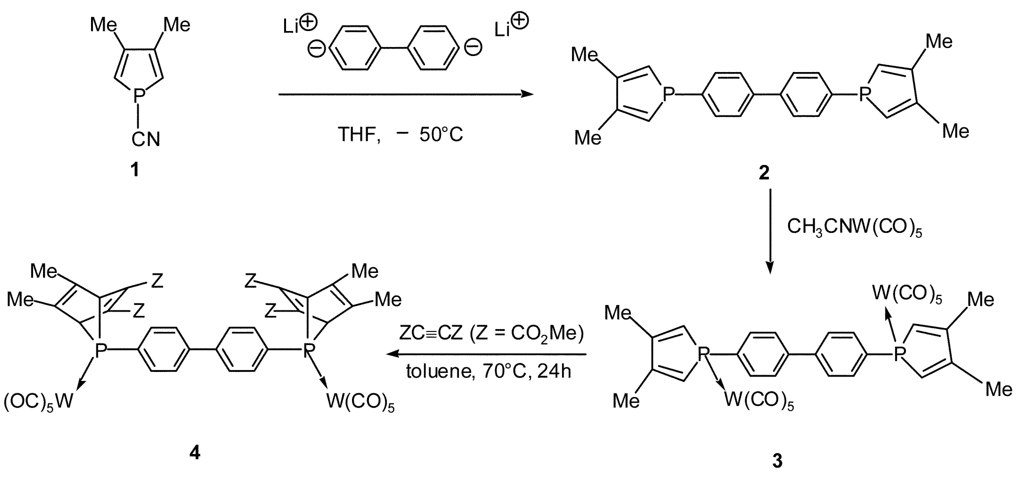
(i) In fact, the parent H–P species exhibits a triplet ground state with a large singlet-triplet gap of 120 kJ mol^{-1}.[18]

(ii) Methylphosphinidene (CH_3–P) also has a triplet ground state which lies about 110 kJ mol^{-1} below the closed-shell singlet.[19] Alkyl derivatives behave in a similar way.

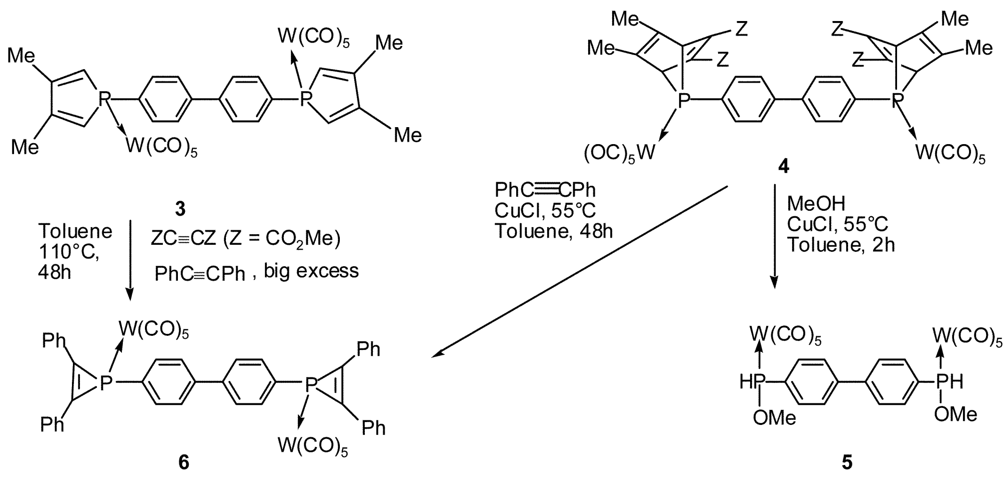
(iii) In phenylphosphinidene (C_6H_5–P), the triplet $^3A_2$ ground state is also well established, followed by a closed-shell singlet (at 0.95 eV or 92 kJ mol^{-1}) and then an open-shell singlet having a similar energy as the closed-shell singlet.[20]

(iv) In the case of *p*-phenyl bis-phosphinidene ($P\text{–}C_6H_4\text{–}P$),[12] where a coupling of both terminal P-electrons through the phenyl ring becomes possible, a quinone-like molecular structure having an open-shell singlet diradical state has effectively been identified as its ground electronic state.[12] In spite of such a large geometric change, the resulting triplet–singlet separation gap is very small, being only 0.077 eV (7 kJ mol^{-1}).

Thus, a question of interest in the BPBP system, is as to whether a strong electron coupling through the biphenyl framework also occurs. In this work, we have adopted a theoretical approach similar to that previously employed for treating phenyl phosphinidene (C_6H_5–P)[20] and *p*-phenyl bis-phosphinidene ($P\text{–}C_6H_4\text{–}P$).[12] In view of the existence of several



(1)



(2)

Table 1 Energies,[a] main electronic configurations and their weights of the three electronic states of BPBP considered

Electronic state	Main electronic configuration	Weight	Natural orbital occupation number	Total energy/au[b] CASSCF(14,14) CASPT2(14,14)	Relative energy/ kJ mol^{-1} [c]
Quintet ^5A	$(b_2)^1(b_3)^1(b_2)^1(b_3)^1$	87%	$(b2)^{1.0}(b3)^{1.0}$	−1140.577207	0
			$(b2)^{1.0}(b3)^{1.0}$	−1142.092954	0
Singlet ^1A_g	$(b_{2g})^2(b_{3g})^2(b_{2u})^0(b_{3u})^0$	13%			
	$(b_{2g})^2(b_{3g})^0(b_{2u})^2(b_{3u})^0$	13%	$(b2g)^{0.9}(b3g)^{1.0}$	−1140.568442	23.0
	$(b_{2g})^0(b_{3g})^2(b_{2u})^0(b_{3u})^2$	18%	$(b2u)^{1.0}(b3u)^{1.1}$	−1142.090722	5.8
	$(b_{2g})^1(b_{3g})^1(b_{2u})^1(b_{3u})^1$	14%			
	$(b_{2g})^0(b_{3g})^0(b_{2u})^2(b_{3u})^2$	18%			
Triplet $^3B_{1u}$	$(b_{2g})^2(b_{3g})^1(b_{2u})^1(b_{3u})^0$	15%	$(b2g)^{0.7}(b3g)^{1.0}$	−1140.558389	49.4
	$(b_{2g})^1(b_{3g})^2(b_{2u})^0(b_{3u})^1$	10%	$(b2u)^{1.0}(b3u)^{1.3}$	−1142.086732	16.3
	$(b_{2g})^0(b_{3g})^1(b_{2u})^1(b_{3u})^2$	41%			
	$(b_{2g})^1(b_{3g})^0(b_{2u})^2(b_{3u})^1$	10%			

[a] Results were obtained from CASSCF(12,12)/6-31G(d) optimised geometries given in Figure 2. [b] Energies calculated at the CASPT2-level using the corresponding CASSCF(14,14) wave-functions, and the 6-31G(d) basis set. [c] The zero-point energies of the states considered are similar amounting to around 424 kJ mol^{-1}. For each state, upper value: CASSCF; lower value: CASPT2.

high spin states (triplet and quintet), multi-reference wave-functions were also constructed for BPBP. In constructing adequately such wave functions, the complete active space self-consistent field method (CASSCF)[17] was used in conjunction with the 6-31G(d) basis set including d-polarization functions on C and P atoms.

The active spaces have been selected as follows: in a BPBP structure, the presence of two phenyl rings generates twelve (12) π-orbitals whereas the two terminal phosphorus atoms bring about four (4) π-orbitals ($3p_x$ and $3p_y$). Thus, a full active space enclosing the whole π-system consists of 16 electrons in 16 orbitals. Nevertheless, such (16,16) CASSCF calculations go far beyond our available computing facilities. The largest active space that could actually be constructed is the (14,14) one.

Let us consider a planar BPBP structure which possesses a D_{2h} point symmetry group and thus involves 8 different irreducible representations in which both representations $a_g(\sigma)$ and $b_{1u}(\sigma)$ correspond to the in-plane orbitals and could thus be excluded. The set of sixteen (16) relevant orbitals includes five (5) b_{2g}, two (2) b_{1g}, one (1) b_{3g}, two (2) a_u, one (1) b_{2u} and five (5) b_{3u} orbitals. From this set, a (14,14) active space has been obtained by removing the lowest-lying occupied b_{3u} and highest-lying unoccupied b_{2g} orbitals. Similarly, a (12,12) active space has been selected excluding the two lowest-lying and two highest-lying (b_{2g} and b_{3u}) orbitals of the 16 orbital set.

The shape of the fourteen (14) active orbitals employed in CASSCF calculations is illustrated in Figure 1. These include the four different combinations of $3p_x(\pi)$ and $3p_y(\sigma)$ orbitals of both phosphorus atoms describing their lone pairs and the π-orbitals arising from the biphenyl skeleton. These are the natural orbitals (NO) obtained from a CASSCF calculation.

Full geometry optimisations for the different electronic states of BPBP have been carried out using the CASSCF(12,12)/6-31G(d) wave functions, that led to either a planar (D_{2h}) or a skewed (D_2) form. Figure 2 displays the selected geometrical parameters of the lowest-lying state in each singlet, triplet and quintet multiplicity. To obtain better estimates for the energy separations between different states, single-point electronic energy computations at the second-order perturbation theory level, CASPT2, were also carried out using the corresponding CASSCF(12,12) and CASSCF(14,14) wave-functions as references, CASSCF(12,12)-optimized geometries and the same basis functions. As mentioned above, due to our limited computational resources, calculations employing larger active spaces and/or basis sets could not be performed. The calculated results are summarized in Table 1 including the important configurations in each electronic state, the orbital occupation numbers derived from CASSCF wave-functions and the corresponding CASSCF/CASPT2 energies.

To simplify the orbital analysis, let us now consider a skewed D_2 conformation of BPBP in which the two phenyl-phosphinidene planes form a dihedral ϕ angle around the central C_1–C_1' bond. Combination of four 3p(P) atomic orbitals leads to four molecular orbitals (MO's) having the b_2 and b_3 symmetry representations. Each occupied orbital could naively be assigned as one phosphorus lone pair. Other combinations of the π-orbitals give rise to different a and b_1 MO's. It turns out that the different lower-lying electronic states of BPBP are basically dominated by varying distributions of the four P lone pair electrons within the four b_2 and b_3 MO's. The shape of the corresponding MO's is similar to those given in Fig. 1. We will consider the electronic states starting with the high spin ones.

Quintet states. At the CASSCF level, the ^5A state is computed to lie well below the planar $^5B_1$ and $^5B_2$ states. Therefore we have considered hereafter only the former state. An equal distribution of four electrons in four b_2 and b_3 MO's results in a *quintet* state ^5A: . . .$(b_2)^1(b_3)^1(b_2)^1(b_3)^1$ which is expected to be the lowest-lying state in this multiplicity. Full geometry optimisations for a ^5A state using the relevant CASSCF(12,12) wave functions lead to a skewed D_2 molecular structure whose selected geometry is displayed in Fig. 2. The CASSCF wave function of this totally symmetrical quintet state is effectively dominated by the Hartree–Fock determinant, with a coefficient of $C_0 = 0.93$. A separate stability test of the UHF determinant pointed out that the latter is stable under all perturbations. To check further this point, geometry optimisations using either UHF or density functional theory (DFT with the B3LYP functional) have also been carried out. Indeed, both methods invariably lead to a D_2 geometry which is quite close to the CASSCF result (*cf.* Fig. 2). Between CASSCF and B3LYP results, the main differences concern the C–P distance (1.823 versus 1.802 Å) and the dihedral angle (45.0° versus 36.4°).

From both geometrical and electronic viewpoints, this quintet state could be regarded as a connection of two triplet phenyl phosphinidene (Ph–P) moieties. The rotation around the central C_1–C_1' bond is a rather facile process with an energy barrier to planarity of a few kJ mol^{-1}. It is clear that in this high spin state, there is no coupling between open-shell electron located at P-atoms.

Triplet states. Distribution of the same four-electrons-in-four-orbitals framework but within the triplet manifold leads to various states. CASSCF(12,12) geometry optimisations reveal that both the twisted ^3A (D_2) and planar $^3B_{1u}$ (D_{2h}) states constitute the two lowest-lying triplet equilibrium structures.

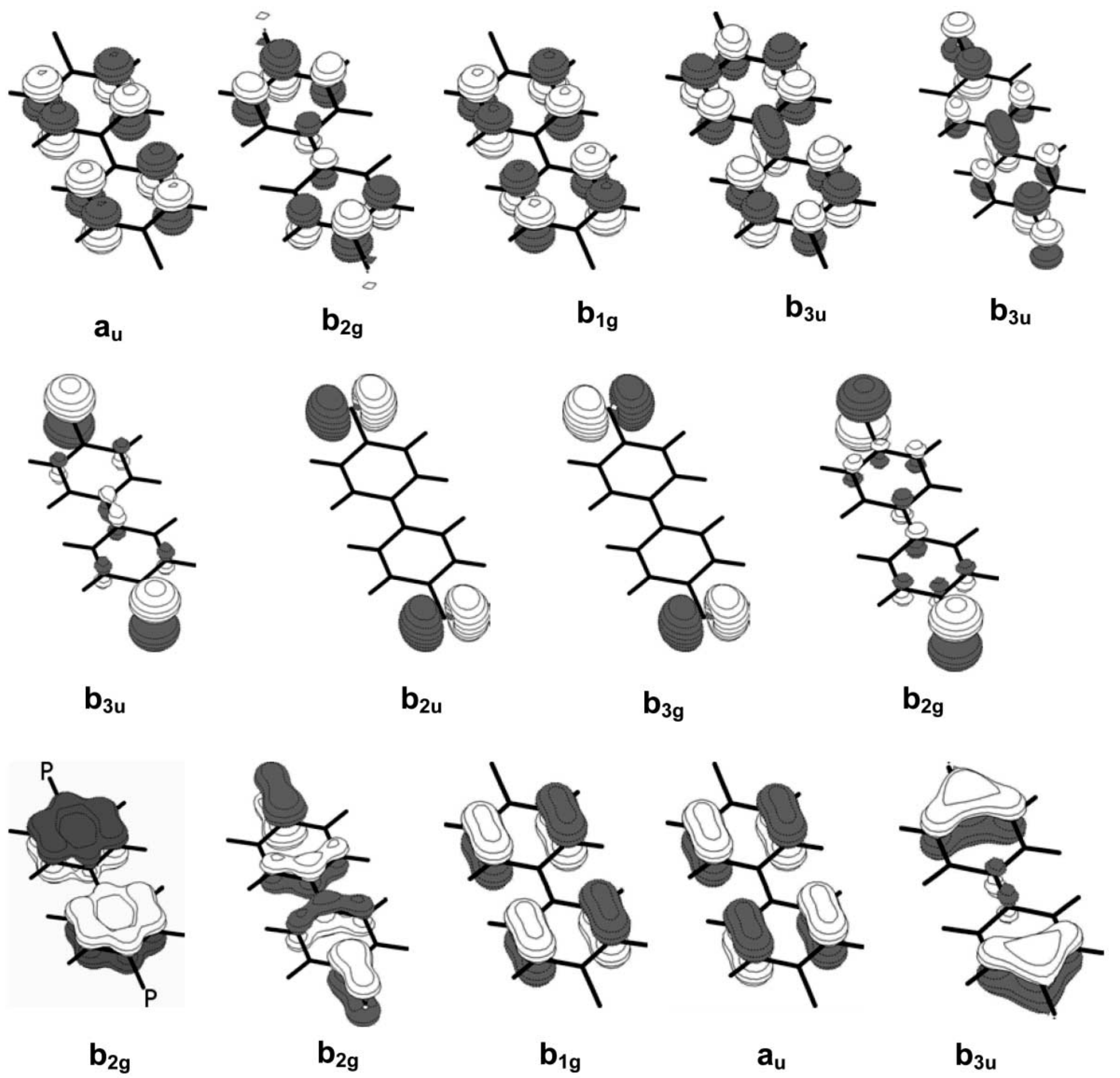


Fig. 1 The shape of the 14 active space orbitals of the 4,4-*p*-biphenyl bis-phosphinidene used in CASSCF/CASPT2 computations. The natural orbitals were obtained from a CASSCF(14,14) wavefunction.

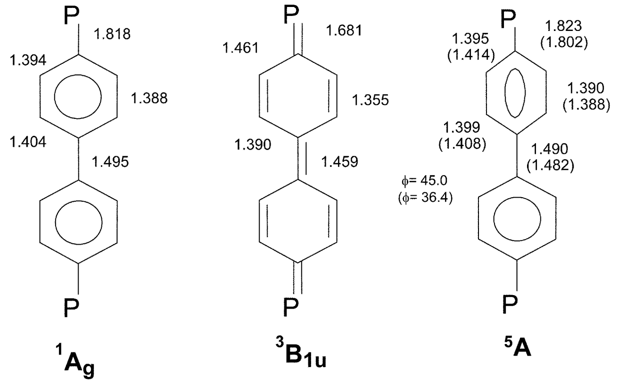


Fig. 2 Selected geometrical parameters of 4,4-*p*-biphenyl bis-phosphinidene in the lowest-lying singlet, triplet and quintet electronic states using CASSCF(12,12)/6-31G(d). Bond lengths are given in angstroms and bond angles in degrees. In parentheses are the values obtained from UB3LYP/6-31G(d) computations for the quintet state.

The wave function of the ^{3}A equilibrium structure is formed from a basic combination of four electronic (orbital) configurations including the following:

$$^3\mathrm{A}\text{: } C_1[\ldots(\mathrm{b}_2)^2(\mathrm{b}_3)^1(\mathrm{b}_3)^1] + C_2[\ldots(\mathrm{b}_3)^2(\mathrm{b}_2)^1(\mathrm{b}_2)^1] + C_3[\ldots(\mathrm{b}_3)^1(\mathrm{b}_3)^1(\mathrm{b}_2)^2] + C_4[\ldots(\mathrm{b}_2)^1(\mathrm{b}_2)^1(\mathrm{b}_3)^2]$$

with almost equal contributions of C_i = 0.45 (weights of about 21% each). In this skewed conformation, the dihedral angle ϕ amounts to about 36°.

CASSCF(12,12) geometry optimisations also give a planar equilibrium structure with a $^3\mathrm{B}_{1\mathrm{u}}$ electronic state with two dominant configurations: $^3\mathrm{B}_{1\mathrm{u}}$: $C_0[\ldots(\mathrm{b}_{3\mathrm{u}})^2(\mathrm{b}_{2\mathrm{u}})^1(\mathrm{b}_{3\mathrm{g}})^1] + C_1[\ldots(\mathrm{b}_{2\mathrm{g}})^2(\mathrm{b}_{2\mathrm{u}})^1(\mathrm{b}_{3\mathrm{g}})^1]$ with $C_0 = 0.63$ (weight = 41%) and $C_1 = 0.38$ (weight = 15%). There is an exchange between both doubly-occupied $\mathrm{b}_{3\mathrm{u}}$ and $\mathrm{b}_{2\mathrm{g}}$ orbitals in going from the first to the second configuration.

More important perhaps is the geometrical change. As seen in Fig. 2, the $^3\mathrm{B}_{1\mathrm{u}}$ state is characterized by a quinone-type geometry in which the central C_1–C_1' bond has now partially double character (1.45 Å), along with the two terminal double C=P bonds. Thus, a strong electron coupling occurs with only one electron left on each P-atom. In this regard, this state is clearly a biradical composed of two phosphaalkene radicals. As a matter of fact, the NO occupation number indicates an electron unity on each of the singly-occupied orbitals.

Of the two triplets considered, the ^{3}A is calculated to be substantially higher in energy than the $^3\mathrm{B}_{1\mathrm{u}}$ counterpart which is considered as the lowest-lying triplet state.

Singlet states. Under this multiplicity, the electrons could form either closed-shell or open-shell configurations. It is worth mentioning that a pure closed-shell singlet state does not exist.

The CASSCF(12,12) method optimises this state to a planar equilibrium form, with a ^1A_g electronic state, in which open-shell configurations have important contributions (*cf.* Table 1).

A lower-lying open-shell singlet state $^1B_1$ of BPBP, which is defined by a combination of four possible orbital configurations enclosing the available b_2 and b_3 orbitals (with an α spin on b_2 and β spin on b_3), has also been located. Of the two singlet structures found, the ^1A_g state has been computed to be lower in energy than the $^1B_1$ counterpart (>1.0 eV using CASSCF(12,12) computations) and constitutes thus the lowest-lying singlet state.

Overall, the CASPT2(14,14)/6-31G(d) computations based on CASSCF(12,12) optimized geometries, have allowed us to identify the lowest-lying state in each multiplicity, namely the ^5A for the quintet, the $^3B_{1u}$ for the triplet, and the ^1A_g for the singlet. The following energy ordering has been established: ^5A (0) < ^1A_g (6) < $^3B_{1u}$ (16), where the energy differences are given in parentheses and in kJ mol^{-1} and obtained from CASPT2-(14,14) computations (*cf.* Table 1, Relative energy, second line). In other words, *the quintet state* ^5A *is found to be the ground electronic state of BPBP*, but the lower-spin states lie quite close in energy. In view of the limitation of the active space and basis functions employed, it can be regarded that the states are nearly degenerate.

The above finding thus constitutes a major difference of BPBP with the homologue *p*-phenyl bis-phosphinidene (P–C_6H_4–P) which exhibits an open-shell singlet diradical ground state and a quinone-like molecular structure.[12] However, the present results on BPBP are consistent with the previous ones if we consider only the singlet ^1A_g and triplet $^3B_{1u}$ states of BPBP where the singlet state is also found to be slightly lower in energy, by 10 kJ mol^{-1}, than the triplet.

The situation in BPBP appears more consistent with that in the parent phenyl phosphinidene (C_6H_5–P) where the triplet $^3A_2$ ground state is established. As stated above, BPBP is merely a loose combination of two phenyl phosphinidene moieties keeping the spin state on the P-atoms intact. This tends to suggest that while in *p*-phenyl bis-phosphinidene (P–C_6H_4–P), the phosphorus lone pair electrons are strongly coupled through the phenyl ring giving rise to a quinone-type geometry, such a coupling between two phenyl phosphinidene units seems to be possible but smaller. In fact, even though the molecular skeleton tends to adopt a planar shape in some states (triplet), the rotation around the dihedral angle ϕ is a quite facile process with a barrier to planarity being less than 10 kJ mol^{-1}. As a result, the ground quintet state adopts a twisted conformation. It is apparently obvious that the longer the chain, the weaker the electron coupling.

Summary

In this combined experimental and theoretical study, we have been able on the one hand, to prepare a versatile precursor for 4,4′-*p*-biphenyl bis-phosphinidene as the bis-tungstenpentacarbonyl complex and to prove its existence by reactions with trapping agents, and on the other hand to determine its electronic ground state by reliable *ab initio* computations at the CASPT2(14,14) level. In its free form, the transient species features a skewed geometry and a quintet ^5A ground electronic state. However, the quintet–singlet–triplet (^5A–^1A_g–$^3B_{1u}$) energy gaps are found to be small amounting to only 6 and 16 kJ mol^{-1}, respectively. These states could be regarded as nearly degenerate. The coupling between phosphorus lone pair electrons through the biphenyl moiety appears thus to be weak. Finally, it is noted that upon complexation with a metal fragment such as $Cr(CO)_5$, or $W(CO)_5$ the resulting terminal phosphinidene complex adopts a closed-shell singlet ground state[21,22] even though the free phosphinidene has either a quintet, triplet or singlet ground state.[22]

Experimental

All reactions were performed under nitrogen; the solvents were purified, dried and degassed by standard techniques, ^1H, ^{13}C and ^{31}P were recorded on a Brucker AC 200SY spectrometer operating at 200.13, 50.32 and 81.01 MHz respectively. All chemical shifts are reported in parts per million downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method.

4,4′-bis-(3,4-dimethylphospholyl)biphenyl (2). The 4,4′-bis-(dilithio)biphenyl was prepared as described in the literature.[16] The resulting solution in Et_2O was allowed to react with 2 equivalents of 1-cyano-3,4-dimethylphosphole [4a] in THF, between −40 °C and room temperature. The 4,4′-bis-(phospholyl)biphenyl **1** was isolated by chromatography on silica gel with hexane/dichloromethane 10/1 as the eluent. A white powder was thus obtained in 50% yield. ^{31}P NMR (CH_2Cl_2): δ −2.8 ppm; ^1H NMR ($CDCl_3$): δ 2.15, 2.16 (s, 12H, Me), 6.52 (d, $^2J_{(H\text{–}P)}$ =38.4 Hz, 4H, =CH–P), 7.45 (m, 8H, biphenyl); ^{13}C NMR ($CDCl_3$): δ 17.81 (s, Me), 127.13 (d, $^2J_{(C\text{–}P)}$ = 7.8 Hz, C_3 biphenyl), 131.58 (d, $^1J_{(C\text{–}P)}$ = 12.1 Hz, C_4 biphenyl), 133.68 (d, $^1J_{(C\text{–}P)}$ = 18.6 Hz, P–CH=), 141.29 (s, C_1 biphenyl), 149.32 (d, $^2J_{(C\text{–}P)}$ = 7.8 Hz, Me–C=); mass spectrum (^{184}W): *m*/*z* 374 (M^+, 100%); elemental analysis (Found: C, 76.83; H, 6.45. Calc. for $C_{24}H_{24}P_2$: C, 77.00; H, 6.41%).

[4,4′-bis-(3,4-dimethylphospholyl)biphenyl]decacarbonylditungsten (3). A solution of **2** (0.75 g, 2 mmol) and $CH_3CNW(CO)_5$ (5 mmol) in 10 ml of acetonitrile was heated at 55 °C for 1 h. The reaction was followed by ^{31}P NMR. The complex **3** was purified by chromatography on SiO_2 with hexane/dichloromethane 5/1 as the eluent: 1.5 g of **3** was isolated as yellow powder (70% yield). ^{31}P NMR ($CDCl_3$): δ 9.38 ppm ($^1J_{(P\text{–}W)}$ =212.55 Hz); ^1H NMR ($CDCl_3$): δ 2.20 (s, 12H, Me), 6.53 (d, 4H, $^2J_{(H\text{–}P)}$ =36.6 Hz, = CH–P), 7.55 (m, 8H, biphenyl); ^{13}C NMR($CDCl_3$): δ 17.32 (d, $^3J_{(C\text{–}P)}$ = 11.4 Hz), 127.58 (d, $^2J_{(C\text{–}P)}$ = 10.4 Hz, C_3 biphenyl), 129.69 (s, C_2 biphenyl), 131.93 (d, $^1J_{(C\text{–}P)}$ = 13.22 Hz, P–CH=), 142.10 (s, C_4 biphenyl), 150.78 (d, $^2J_{(C\text{–}P)}$ = 9.07 Hz, Me–C=), 196.30 (d, $^2J_{(C\text{–}P)}$ = 63 Hz, *cis* CO), 198.95 (d, $^2J_{(C\text{–}P)}$ = 193 Hz, *trans* CO); mass spectrum (^{184}W): *m*/*z* 1024 ($M^+ + 2$, 55%), 940 ($M^+ - 3CO$, 48%), 884 ($M^+ - 5CO$, 67%), 856 ($M^+ - 6CO$, 29%), 799 (M^+, 45%), 741 ($M^+ - 10CO$, 100%).

[4,4′-bis-(2,3-bis-methoxycarbonyl-5,6-dimethyl-7-phospha-norbornadien-7-yl)-biphenyl]decacarbonylditungsten (4). A solution of **3** (2 g, 2 mmol) and dimethylacetylenedicarboxylate (2 ml) in 5 ml of toluene was heated at 70 °C for 24 h. The product was purified by chromatography on silica gel with hexane/dichloromethane as the eluent (yield 50%). ^{31}P NMR (toluene): δ 208.35 ppm ($^1J_{(P\text{–}W)}$ = 239.2 Hz), ^1H NMR ($CDCl_3$): δ 2.08 (s, 12H, Me), 3.70 (s, 12H, OMe), 4.03 (s, b, 4H, P–CH), 7.17, 7.67 (m, 8H, biphenyl), ^{13}C NMR ($CDCl_3$): δ 16.11 (s, Me), 54.41 (s, OMe), 59.99 (d, $^1J_{(C\text{–}P)}$ =20.6 Hz, P–CH), 127.06 (d, $^3J_{(C\text{–}P)}$ =7.3 Hz, C_2 biphenyl), 128.84 (d, $^2J_{(C\text{–}P)}$ =9.4 Hz, C_3 biphenyl), 138.23 (d, $^1J_{(C\text{–}P)}$ = 16.9 Hz, C_4 biphenyl), 140.67 (d, $^2J_{(C\text{–}P)}$ = 13.9 Hz, =C–Me), 140.95 (s, C_1 biphenyl), 145.81 (d, $^2J_{(C\text{–}P)}$ = 4.2 Hz, C–CO_2Me), 164.82 (s, CO_2Me), 195.89 (d, $^2J_{(C\text{–}P)}$ = 6.2 Hz, *cis* CO), 198.51 (d, $^2J_{(C\text{–}P)}$ =25.0 Hz, *trans* CO).

[4,4′-bis-(methoxyphosphine)biphenyl]decacarbonylditungsten (5). A solution of **4** (0.4 g, 0.3 mmol), CuCl (20 mg), MeOH in excess (1 ml) in 8 ml of toluene was heated at 55 °C for 2 h. The product was purified by chromatography on silica gel with hexane/dichloromethane 4/1 as the eluent. 200 mg of **5** was isolated as a white powder (yield 72%). ^{31}P NMR ($CDCl_3$): δ 106.56 ($^1J_{(P\text{–}W)}$ = 280.5 Hz, $^1J_{(P\text{–}H)}$ = 355.4 Hz), ^1H NMR

($CDCl_3$): δ 3.48 (d, 6H, $^3J_{(P-H)}$ = 12.5 Hz, OMe), 7.7 (m, 8H, biphenyl), 7.97 (d, 2H, $^1J_{(P-H)}$ = 344.28 Hz, P–H), ^{13}C NMR ($CDCl_3$): δ 58.95 (d, $^2J_{(C-P)}$ = 14.5 Hz, O–Me), 126.80, 129.96 (d, $^2J_{(C-P)}$ =12.10 Hz, $^3J_{(C-P)}$ = 9.36 Hz, C_2, C_3, C_5, C_6 biphenyl), 133.51 (d, $^1J_{(P-C)}$ = 40.8 Hz, C *ipso*), 141.70 (s, C_1), 194.40 (d, $^2J_{(P-C)}$ = 7.90 Hz, *cis* CO), 198.10 (d, $^2J_{(P-C)}$ = 26.03 Hz, *trans* CO), mass spectrum (^{184}W): *m*/*z* 928 ($M^+ + 2$, 50%), 872 ($M^+ - 2CO$, 35%), 787 (M^+-5CO, 100%), elemental analysis (Found: C, 31.29, H, 1.81. Calc. for $C_{24}H_{16}O_{12}P_2W_2$: C, 31.13, H, 1.74%).

[4,4′-bis-(2,3-diphenylphosphiren-1-yl)-biphenyl]decacarbonylditungsten (6). Method A: A solution of **4** (0.4 g, 0.3 mmol), CuCl (20 mg), diphenylacetylene in excess (800 mg, ≈3 mmol) in 10 ml of toluene was heated at 55 °C for 48 h. The product was purified by chromatography on silica gel with hexane/dichloromethane 10/6 as the eluent. 210 mg of **6** was isolated as a white powder (60% yield).

Method B: A solution of **3** (1 g, ≈1 mmol), dimethylacetylene dicarboxylate in excess (1.5 ml, ≈10 mmol), diphenylacetylene in excess (2.5 g, ≈10 mmol) in 10ml of toluene was heated at 110 °C for 48 h. After purification on silica gel, 650 mg of **6** was isolated (60% yield).

^{31}P NMR ($CDCl_3$): δ −161.13 $^1J_{(P-W)}$ = 269.27 Hz); ^{1}H NMR ($CDCl_3$): δ 7.44, 7.82 (m, biphenyl, phenyl); ^{13}C NMR ($CDCl_3$): δ 127.8 (d, $^1J_{(C-P)}$ = 6.36 Hz, phosphirene ring) 128.01, 129.10 (d, $^3J_{(C-P)}$ = 9.33 Hz, $^2J_{(C-P)}$ = 10.46 Hz, C_2, C_3, C_5, C_6 biphenyl), 130.06, 131.07, 132.28 (phenyl), 137.71 (d, $^2J_{(C-P)}$ = 5.18 Hz, C phenyl), 142.74 (s, C_1 biphenyl), 196.55 (d, $^2J_{(C-P)}$ =8.20 Hz, *cis* CO),198.31 (d, $^2J_{(C-P)}$ = 31.06 Hz, *trans* CO); elemental analysis (Found C, 49.68; H, 2.41. Calc. for $C_{50}H_{28}O_{10}P_2W_2$: C, 49.29; H, 2.32%).

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