3154 *Inorg. Chem.* **1998,** *37,* 3154−3158

Synthesis, Unusual Trigonal Prismatic Geometry, and Theoretical Study of the Homoleptic Tris-(2,2′-biphosphinine) Complexes of Chromium, Molybdenum, and Tungsten

Patrick Rosa,[†] Louis Ricard,[†] Pascal Le Floch,*[,†] François Mathey,*[,†] Gjergji Sini,[‡] and Odile Eisenstein*[,§]

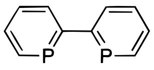
Laboratoire “Hétéroéléments et Coordination”, URA CNRS 1499, Ecole Polytechnique,
91128 Palaiseau Cedex, France, Bâtiment des Sciences de la Matière, 5 Mail Gay Lussac, Neuville sur
Oise, 95031 Cergy Pontoise Cedex, France, and LSDSMS (UMR5636), Case Courrier 14, Université de
Montpellier 2, 34095 Montpellier Cedex 5, France

Received January 14, 1998

The preparation of homoleptic tris-(4,4′,5,5′-tetramethyl-2,2′-biphosphinine) complexes of chromium **2**, molybdenum **3**, and tungsten **4** [M(tmbp)$_3$] is described. These complexes can be obtained by the simple reduction of $CrCl_3$·3THF, $MoCl_5$, and WCl_6, respectively, with magnesium in the presence of the ligand. The tungsten complex **4** was alternatively prepared in better yields by the reduction of the [$WBr_4(MeCN)_2$] complex with zinc dust. The structure of **4** has been unambiguously confirmed by an X-ray crystal structure analysis. Surprisingly, whereas an octahedral geometry ($\theta = 60°$) would have been expected for a d^6 ML$_6$, complex **4** presents a nearly trigonal prismatic structure ($\theta = 15°$). Two data reveal that a significant electronic transfer from the metal to the ligand occurs: short P−W bond distances (2.35−2.36 Å) and a shortened C−C bridge (1.442(4) Å) between two phosphinine subunits. Ab initio calculations at the DFT(B3LYP) level have been undertaken to rationalize this deviation from the ideal octahedral geometry. The geometry of [$W(P_2C_2H_4)_3$], which was chosen as a model for **4**, and that of the d^0 ML$_6$ tris-(dithiolene) complex [$W(S_2C_2H_4)_3$], which is known to be trigonal prismatic, have been calculated. In both cases the calculated geometries are in good agreement with the corresponding observed data. On the basis of these results it is suggested that [$W(P_2C_2H_4)_3$] can be most conveniently described as a fully oxidized d^0 complex in which the phosphorus P lone pairs are conjugated to the C═C double bond and not bonded to the metal center.

Introduction

So far, the coordination chemistry of planar delocalized nitrogen ligands and edifices has no parallel in phosphorus chemistry. Over the last two decades, a great deal of effort has been devoted to the synthesis of various sophisticated ligands having, as subunits, phosphorus equivalents of the most usual structures such as imines (phosphaalkenes),[1] pyrrolyl anions (phospholyl anions),[2] and pyridines (phosphinines).[3] It now appears that a better understanding of the electronic properties of these ligands and their complexes is a prerequisite to their involvement in more applied projects. In 1991, we synthesized the first 2,2′-biphosphinine,[4] the phosphorus equivalents of 2,2′-bipyridines; since then, we have been interested in their coordination chemistry.[3a]



2,2'-biphosphinine

In previous reports, we showed that these molecules behave as poorer σ-donor and better π-acceptor ligands than their nitrogen counterparts. Quite logically, they prove to be powerful chelates for the stabilization of electron-rich complexes. This was illustrated recently by the synthesis of highly stable [Ru^{II}(η^5-C$_5$Me$_5$)Cl][5] and homoleptic Ni^0 complexes.[6] On the other hand, it appeared that the coordination to electrophilic metal centers tends to partially dearomatize the ligand which then reacts with protic reagents.[7] An illustration of this behavior was found while trying to synthesize the dicationic [Ru(2,2′-biphosphinine)$_3$]$^{2+}$ complex which proved not to be viable.[5,8] Given the utmost importance of [Ru(bpy)$_3$]$^{2+}$ as a photosensitizer,[9] we decided to investigate the synthesis of isolelectronic homoleptic

---

* Corresponding authors.

[†] Ecole Polytechnic.

[‡] University of Cergy-Pontoise.

[§] University of Montpellier.

(1) (a) Jouaiti, A.; Geoffroy, M.; Bernardinelli, G. *Tetrahedron Lett.* **1982**, *33*, 5071. (b) Jouaiti, A.; Geoffroy, M.; Terron, M.; Bernardinelli, G. *J. Chem. Soc., Chem. Commun.* **1995**, *117*, 2251. (c) van der Sluis, M.; Wit, J. B. M.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 174. (d) van der Sluis, M.; Beverwijk, V.; Termaten, A.; Gavrilova, E.; Bickelhaupt, F.; Koojman, H.; Veldman, N.; Spek, A. L. *Organometallics* **1997**, *16*, 1144.

(2) (a) (review) Mathey, F.; *Coord. Chem. Rev.* **1994**, *137*, 1. (b) Holand, S.; Jeanjean, M.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 98.

(3) (a) (review) Mathey, F.; Le Floch, P. *Chem. Ber.* **1996**, *129*, 263.(b) Waschbüsch, K.; Le Floch, P.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, *132*, 910.

(4) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1991**, *113*, 667.

(5) Le Floch, P.; Mansuy, S.; Ricard, L.; Mathey, F.; Jutand, A.; Amatore, C. *Organometallics* **1996**, *15*, 3267.

(6) Le Floch, P.; Ricard, L.; Mathey, F.; Jutand, A.; Amatore, C. *Inorg. Chem.* **1995**, *34*, 11.

(7) (a) Schmid, B.; Venanzi, L. M.; Albinati, A.; Mathey, F. *Inorg. Chem.* **1991**, *30*, 4693. (b) Carmichael, D.; Le Floch, P. Mathey, F. *Phosphorus Sulfur* **1993**, *77*, 255.

(8) Carmichael, D.; Le Floch, P.; Ricard, L.; Mathey, F. *Inorg. Chim. Acta* **1992**, *198−200*, 437.

S0020-1669(98)00042-1 CCC: $15.00

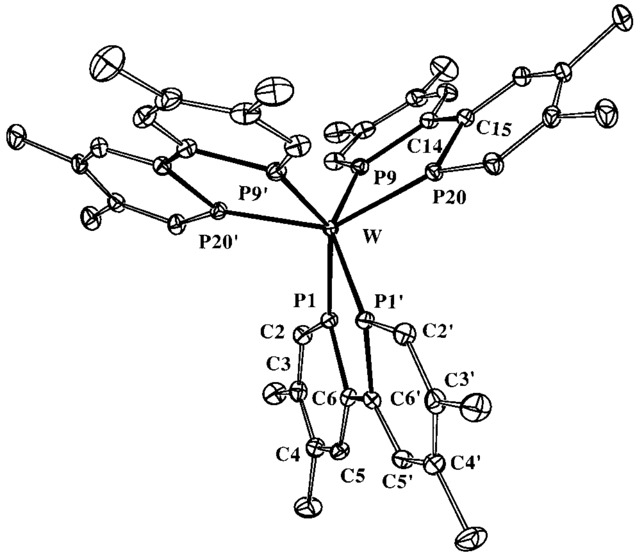
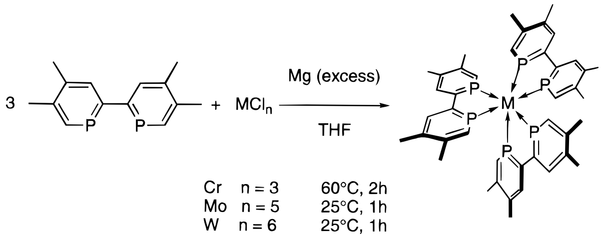


Figure 1. ORTEP drawing of one molecule of **4**. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): W−P(1) 2.3552(9), W−P(9) 2.361(1), W−P(20′) 2.3640(6), P(1)−C(2) 1.726(3), P(1)−C(6) 1.742(3), C(2)−C(3) 1.374(5), C(3)−C(4) 1.414(5), C(4)−C(5) 1.392(5), C(5)−C(6) 1.405(4), C(6)−C(6′) 1.442(4), C(14)−C(15) 1.446(4). Selected bond angles (deg): P(1)−W−P(9) 89.60(3), P(1)−W−P(20) 122.16(3), P(9)−W−P(20) 74.23(3), W−P(1)−C(2) 136.5(1), W−P(1)−C(6) 119.2(1), W−P(9)−C(14) 118.9(1), C(2)−P(1)−C(6) 103.5(1), P(1)−C(6)−C(6′) 113.6(2), P(9)−C(14)−C(15) 113.6(3).

complexes of group 6 metals [M(2,2′-biphosphinine)$_3$] (M = Cr, Mo, or W), which should be stable in view of the existence of [Cr(phosphinine)$_6$].[10] In this paper, we report the successful synthesis of these complexes as well as ab initio calculations within the DFT(B3LYP) framework, which provide an interpretation for the unusual trigonal prismatic structure of these formally d^6 hexacoordinated complexes.

Results and Discussion

Synthesis. All our work was conducted with the readily available 4,4′,5,5′-tetramethyl-2′,2′-biphosphinine (tmbp).[4,11] The desired complexes were easily obtained using a conventional reductive pathway. The corresponding metal halides ($CrCl_3$·3THF, $MoCl_5$, and WCl_6) were reacted with excess magnesium powder in the presence of 3 equiv of ligand in THF at room temperature (eq 1).



(1)

2 (65%)
3 (50%)
4 (35%)

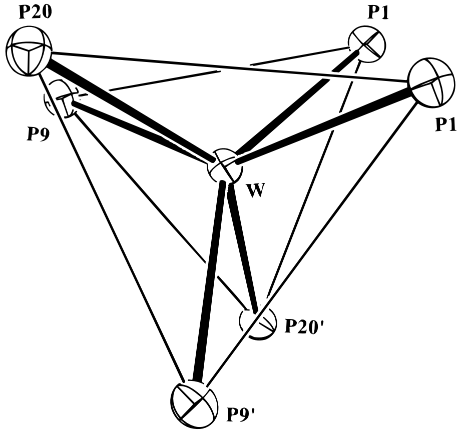
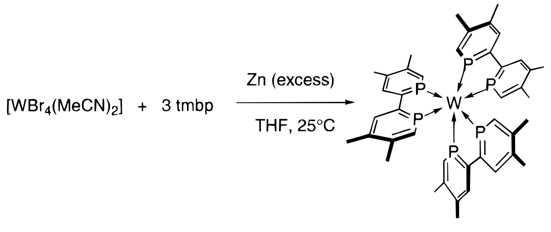


Figure 2. ORTEP view of **4** showing the twist angle between the two P_3 triangles.

Quite interestingly, we found that all of these reactions proceeded more smoothly under nitrogen than under argon. Although no intermediates could be detected by ^{31}P NMR monitoring, it is likely that dinitrogen complexes such as [M(tmbp)$_2$(N$_2$)$_2$] are involved during the course of the reduction. Our opinion is supported by the fact that similar species were isolated in the case of molybdenum and tungsten with 1,2-bis(diphenylphosphino)ethane as ligand.[12] All complexes **2**−**4** were obtained after a simple filtration as deep-purple solids in fair yields. Interestingly, the UV spectrum of **4** in THF displays an intense absorption at 550 nm (ϵ 2.15 × 10^4) which deserves further investigation. Whereas the chromium derivative **2** turned out to be somewhat unstable, the molybdenum and tungsten species **3** and **4** are in air. All of them were fully characterized by ^1H and ^{31}P NMR spectroscopy and by elemental analysis for complexes **3** and **4**. In view of further investigation, we tried to improve the synthesis of **4**. The reduction of a tungsten tetrabromide precursor by zinc dust proved to be substantially better (eq 2).



(2)

4 (65%)

X-ray Diffraction Study. Single crystals of **4**, suitable for X-ray diffraction analysis, were obtained by slow diffusion of ether into a THF solution of the complex at room temperature. ORTEP views of **4** are presented in Figures 1 and 2. Many features make this structure quite remarkable. Contrary to what is expected for a d^6 ML$_6$ complex, the geometry of complex **4** is not octahedral but nearly trigonal prismatic. To the best of our knowledge, this is the first known example of a group 6 formally d^6 metal complex having η^1-P ligands displaying such a deviation. As shown in Figure 2, the most convenient way to describe the structure of **4** is to consider a "pseudo" D_3 symmetry. The phosphorus atoms P_1, P_9, and $P_{20'}$ and $P_{1'}$, P_{20}, and $P_{9'}$ draw two P_3 triangles which lie in approximately parallel planes (dihedral angle = 0.17 ± 0.02°). The twist angle (θ) formed by the two medians of each triangle conveniently reflects the distortion from O_h octahedral ($\theta = 60°$) to D_{3h} trigonal

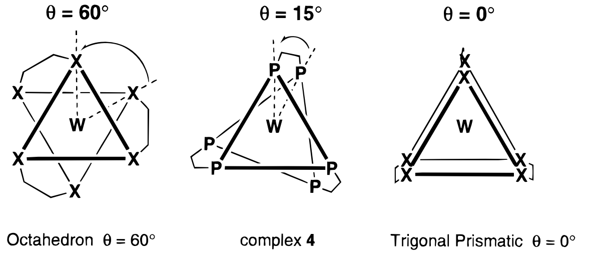
---

(9) Juris, A.; Balzani, V.; Barigiletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(10) Elschenbroich, C.; Nowotny, M.; Kroker, J.; Behrendt, A.; Massa, W.; Wocaldo, S. *J. Organomet. Chem.* **1993**, *459*, 157.

(11) Le Floch, P.; Ricard, L.; Mathey, F. *Bull. Soc. Chim. Fr.* **1994**, *131*, 330.

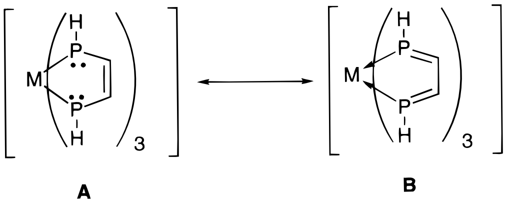
(12) (a) Bell, B.; Chatt, J.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2492. (b) George, J. A.; Seibold, C. D. *Inorg. Chem.* **1973**, *12*, 2544 and 2549.



Octahedron θ = 60° complex **4** Trigonal Prismatic θ = 0°

Figure 3. Structures of [M(chelating ligand)$_3$] complexes showing the deviation from octahedral to trigonal prismatic geometries.

Scheme 1. Two Mesomeric Formula Illustrating the Bonding Modes of $P_2C_2H_4$ to a Transition Metal[a]



[a] Formula A: (1 + 1) electron donation from the ligand to the metal (oxidation state +6). Formula B: (2 + 2) electron donation (oxidation state 0).

prismatic ($\theta = 0°$) geometries. In fact, the geometry of **4** ($\theta = 15 \pm 0.6°$) is very close to those recorded for tris(dithiolene) complexes of Mo(IV) and W(IV) with θ ca. 28° (see Figure 3).[13]

Since [Cr(phosphinine)$_6$][10] displays a perfect octahedral geometry, it is clear that the chelation induces some drastic changes in the electronic structure of **4**. Some insight can be gained from an inspection of the geometrical parameters of the C_2P_2W chelate rings. On one hand, a relevant piece of data concerns the P−W bond lengths at 2.35−2.36 Å which appear to be significantly shorter in **4** than in the [W(CO)$_5$(2-chlorophosphinine)] complex:[14] d(P−W) = 2.457(2) Å. On the other hand, the internal P═C bonds are very slightly lengthened by the complexation: 1.742(3) Å in **4** vs 1.736(4) Å in the free *cis*-tmbp. Finally, the most important information is provided by the shortening of the C−C bridge between the two phosphinine subunits: d(C_6−$C_{6'}$) = 1.442(4) Å vs 1.490(8) Å in the free *cis*-tmbp.[15] All of these observations suggest a sizable electronic delocalization within the chelate ring. The π^* lowest unoccupied molecular orbital (LUMO) of biphosphinines is P−C antibonding and C−C bonding. Thus, the electronic transfer from the metal to the LUMO of the ligand is expected to shorten the bridge. It must be stressed here that such a delocalization is much weaker in the [Cr(CO)$_4$(tmbp)][4] complex since the presence of carbonyls decreases the ability of the metal to give electrons to tmbp.

Theoretical Calculations. The model systems [M($P_2C_2H_4$)$_3$] (M = Mo, W) (see Scheme 1) were optimized by ab initio calculations at the DFT(B3LYP) level.[16] Since the geometries are similar for Mo and W, we will discuss only [W($P_2C_2H_4$)$_3$] for the sake of comparison with the experimental data.

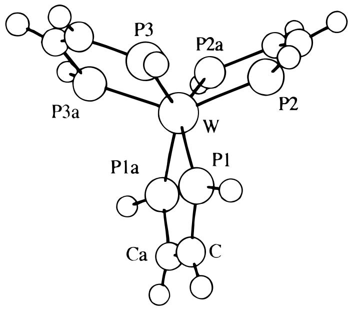


Figure 4. DFT(B3LYP)-optimized structure of [W($P_2C_2H_4$)$_3$]. Distances in Å, angles in degrees. W−P 2.410, P−C 1.752, C−C 1.390, P(1)−W−P(1a) 75.1, P(1)−W−P(2) 87.3, P(1)−W−P(2a) (P3a) or P(1a)−W−P(2) or (P3) average 132, W−P−C 116.0, P−C−C 116.0.

[W($P_2C_2H_4$)$_3$] is a slightly distorted trigonal prism with essentially C_3 symmetry. A view of the calculated structure is presented in Figure 4. Defining θ as in Figure 3, the octahedral structure corresponds to $\theta = 60°$ and the ideal prism to 0°. The present calculated structure ($\theta = 11°$) is thus much closer to the prismatic geometry in full agreement with the solid-state structure of **4** ($\theta = 15°$). In particular, this shows that the aromatic backbone of the biphosphinine ligand is not a prerequisite for the observed geometry. All calculated structural parameters agree well with the corresponding observed data.

The W−P distances at 2.410 Å are slightly longer than the experimental values as is often the case for calculated metal−P distances. Whereas the P−C distance of 1.752 Å is very close to the experimental value (1.742 Å), the C−C distance of 1.389 Å appears to be significantly shorter than the experimental one (1.447 Å). This can be attributed to the lack of the two aromatic rings in the model chosen for the calculations. The bite angle P1−W−P1a is very close to the experimental value (calculated 75° vs 74.25°). Within a triangular face, the average P−W−P angle is 87.3° which compares well to the experimental 89.6°. This good agreement between calculated and experimental parameters suggests that our simplified model mimics well the real biphosphinine ligand. It was also verified that an octahedral structure is not a secondary minimum on the potential energy surface. The equivalent Mo complex is calculated to have a similar structure with θ equal to 13° showing that the prismatic structure is not specific to the W metal.

To what extent is the nature of the biphosphinine ligand responsible for the observed geometry through subtle angular constraints? The [Cr(CO)$_4$(biphosphinine)][4] ligand has an octahedral structure with a bite P−M−P angle (77.15(3)°) very close to that in **4** (74.23(3)°). Furthermore, other complexes having similar linkages around the metal and within the ligands (such as the[Ru(bpy)$_3$]$^{2+}$) take an octahedral geometry.[17]

The prismatic structure for a formally d^6 hexacoordinated complex is certainly unexpected, and it is thus necessary to return to the factors which favor a prismatic structure for hexacoordination. The first trigonal prismatic complex in group 6 is a tris(dithiolene)−Mo complex reported by Schrauzer et al.[18] We have thus calculated this species with the same level of theory as previously in order to identify the factors which favor this geometry.

---

[13] Brown, G. F.; Stieffel, E. *Inorg. Chem.* **1973**, *12*, 2140.

[14] Le Floch, P.; Ricard, L.; Mathey, F. *Polyhedron* **1990**, *9*, 991.

[15] Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F.; Jutand, A.; Amatore, C. *Organometallics* **1992**, *11*, 2475.

[16] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian94, Revision D.2*; Gaussian, Inc.: Pittsburgh, PA, 1995.

[17] (a) Rillema, D. P.; Jones, D. S.; Levy, H. *Inorg. Chem.* **1979**, 849. (b) Biner, M.; Bürgi H.-B.; Ludi, A.; Röhr, C. *J. Am. Chem. Soc.* **1992**, *114*, 4, 5197.

[18] Smith, E. A.; Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc.* **1965**, *87*, 5798.

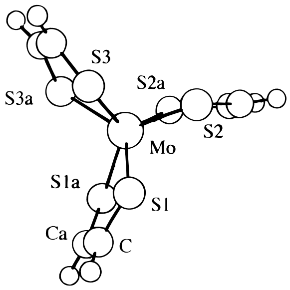


Figure 5. DFT(B3LYP)-optimized structure of [Mo($S_2C_2H_2$)$_3$]. Distances in Å, angles in degrees. Mo−S 2.425, S−C 1.718, C−C 1.370, S(1)−Mo−S(1a) 82.0, S(1)−Mo−S(2) 81.7, Mo−S−C 106.1, S−C−C 121.8.

[Mo($S_2C_2H_2$)$_3$] has a perfect trigonal prismatic structure ($\theta = 0°$). A view of the calculated structure is presented in Figure 5. The Mo−S distances of 2.425 Å are longer than the experimental value (2.33 Å ± 0.02) but remain reasonably close in consideration of the high standard deviation on this distance. The S−C and the C−C distances at 1.717 and 1.370 Å, respectively, compare favorably with those found experimentally (1.70 and 1.34 Å). The angular parameters around the Mo atom are properly mimicked (calculated angle between Mo−S bonds is equal to 82° for S belonging to different triangular faces and 81.7° for S belonging to the same face vs 82.5° for all S in the experimental system). As in the experimental structure, the carbon atoms are not in the plane passing through the Mo and S atoms but deviate by 12° (18° from the X-ray structure). There is thus a good agreement between experimental results and the theoretically optimized structure.

It is highly paradoxical that the biphosphinine complex **4** has a structure very close to that of [Mo(dithiolene)$_3$] which is commonly viewed as a Mo(VI) d^0 complex, while an octahedral geometry would have been expected with the traditional electron counting of a d^6 ML_6 complex. This suggests that **4** cannot be regarded as a conventional W(0) complex. In the extreme, could it be viewed as a d^0 W(VI) complex? The structure of hexacoordinated d^0 complexes[19] has raised considerable controversy mostly among theoreticians.[20] It is now currently accepted that removing electrons from the t_{2g} π-symmetry nonbonding orbital of an octahedron results in distortion which can take various facets, depending on the nature of the ligand. In the total absence of π-donating ligands, the geometry is trigonal prismatic as first predicted by the calculations[20] and verified experimentaly by electron diffraction[21a] and X-ray crystal determination[21b,c] for WMe_6. When π donors are introduced, changes in the structures have been observed. However, in the [Mo(dithiolene)$_3$], θ is equal to 0° since the lone pair of each S atom is delocalized on the C═C double bond and thus behaves as a poor donor to the metal. In contrast, in the [W(tris(pinacolate)$_3$] complex where the lone pairs of the oxygens are not conjugated with the C═C double bond, θ takes a value of 34°.[20i] Alternative structures can also be observed such as in the case of [Ta(OR)$_2$H$_2$X(PR$_3$)] (X = OR, Cl).[20m] When ligands carry numerous lone pairs as in WCl_6 and WF_6, an octahedral geometry is obtained.[22]

If we admit that there is a relationship between formal electron count at the metal and coordination geometry, the complex [W($P_2C_2H_4$)$_3$] is thus closer to a d^0 than to a d^6 complex (formula A). However, this viewpoint does not suggest an ionic bonding between the metal and the ligand but a still covalent situation in which the electrons are partly localized on the $P_2C_2H_4$ ligands in preference to the metal center. The best valence description of the ligand is that of phosphorus P lone pairs conjugated with a C═C double bond and not bonded to the metal center. This preferential electron occupancy, due to the low-lying $\pi^*_{P=C}$ orbital,[23] has produced an internal oxidation of the metal. The P═C−C═P moiety is an even more powerful electron acceptor since its LUMO is the in-phase combination of the two $\pi^*_{P=C}$ orbitals. Placing electrons in the LUMO of P═C−C═P should thus shorten the C−C bond. This explains the short C−C distances calculated for [W($P_2C_2H_4$)$_3$] (1.389 Å) and [Mo($S_2C_2H_2$)$_3$] (1.370 Å) since the π orbitals of the two ligands are occupied by the same number of electrons. In the biphosphinine complex **4**, this C═C double bond is delocalized into the attached aromatic ring and is thus much longer than the calculated value.

In conclusion, it is clear that the [M(tmbp)$_3$] complexes **2**−**4** are most conveniently described as partly oxidized d^{6-n}[M^n(tmbp)$_3^{n-}$] complexes. Their particular electronic structure probably underlies non classical redox and photochemical properties.

Experimental Section

Starting Materials and General Procedures. All reactions were routinely performed under an inert atmosphere of nitrogen or argon by using Schlenk techniques and dry deoxygenated solvents. Dry THF, hexane, and pentane were obtained by distillation from Na/benzophenone, dry CH_2Cl_2 and MeCN by distillation from P_2O_5, and dry DMF by distillation over molecular sieves. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in hertz. The following abbreviations are used: s, singlet; b, broad. Elemental analyses were performed by the “Service d’analyze du CNRS”, at Gif sur Yvette, France. [$CrCl_3$ (THF)$_3$][24] and [WBr_4(MeCN)$_2$][25] were prepared according to published procedures.

Preparation of the [Cr(tmbp)$_3$] Complex (2). Magnesium powder (0.19 g, 8 mmol) and tmbp (0.49 g, 2 mmol) were added to a solution of [$CrCl_3$(THF)$_3$] (0.32 g, 0.85 mmol) in THF (30 mL). The reaction

---

(19) Reviews including leading references: (a) Eisenberg, G. *Prog. Inorg. Chem.* **1970**, *12*, 295. (b) Wentworth, R. A. D. *Coord. Chem. Rev.* **1972**, *9*, 171.

(20) (a) Hoffmann, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484. (b) Demolliens, A.; Jean, Y.; Eisenstein, O. *Organometallics* **1986**, *5*, 1457. (c) Cameron, A. D.; Fitzgerald, G.; Zerner, M. C. *Inorg. Chem.* **1988**, *27*, 3437. (d) Kang, S. K.; Albright, T. A.; Eisenstein, O. *Inorg. Chem.* **1989**, *28*, 1611. (e) Marsden, C. J.; Wolynec, P. P. *Inorg. Chem.* **1991**, *30*, 1681. (f) Jonas, V.; Frenking, G.; Gauss, J. *Chem. Phys. Lett.* **1992**, *194*, 109. (g) Zyubin, A. S.; Musaev, D. G.; Charkin, O. P. Zhu. *Neorg. Khim.* **1992**, *37*, 2345. (h) Shen, M. Z.; Schaefer, H. F.; Partridge, H. *J. Chem. Phys.* **1993**, *98*, 508. (i) Chisholm, M. H.; Parkin, I. P.; Streib, W. E.; Eisenstein, O. *Inorg. Chem.* **1994**, *33*, 812. (j) Landis, C. R.; Cleveland, T.; Firman, T. K. *Science* **1996**, *272*, 182. (k) Kang, S. K.; Tang, H.; Albright, T. A. *J. Am. Chem. Soc.* **1993**, *115*, 1971. (l) Kaupp, M. *J. Am. Chem. Soc.* **1996**, *118*, 3018. (m) Clark, J. R.; Pulvirenti, A. L.; Fanwick, P. E.; Sigalas, M.; Eisenstein, O.; Rothwell, I. P. *Inorg. Chem.* **1997**, *36*, 3623.

(21) (a) Haaland, A.; Hammel, A.; Rypdal, K.; Volden, H. V. *J. Am. Chem. Soc.* **1990**, *112*, 4547. (b) Pfenning, V.; Seppelt, K. *Science* **1996**, *271*, 616. (c) Seppelt, K. *Science* **1996**, *272*, 182.

(22) (a) Haaland, A.; Martinsen, K. G.; Shlykov, S. *Acta Chem. Scand.* **1992**, *46*, 1208. (b) Marx, R.; Seppelt, K.; Ibberson, R. M. *J. Chem. Phys.* **1996**, *104*, 7658.

(23) (a) Schoeller, W. W. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, 1990; p 221. (b) Gilheany, D. G. In *The Chemistry of Organophosphorus Compounds;* Hartley, F. R., Ed.; John Wiley and Sons: New York, 1990; Patai Series, Vol. 1, Chapter 2, p 44 and references therein.

(24) Ocone, L. R.; Block, B. P. *Inorg. Synth.* **1966**, *8*, 150.

(25) Schaefer, M. A.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1972.

mixture was then stirred at 60 °C. After 2 h, a ^{31}P NMR control indicated the completion of the complexation. The dark-red solution obtained was then dried before dichloromethane (50 mL) was added. The solution obtained was then filtered as fast as possible on Celite. After the evaporation of dichloromethane, the deep-purple complex **2** obtained was washed twice with dry hexane (2 × 10 mL) to remove traces of unreacted tmbp and then dried in vacuo. Yield: 0.34 g (65%). ^{31}P NMR (C_4D_8O): δ 253.17. ^{1}H NMR ($CDCl_3$): δ 2.35 (bs, 36H, Me), 8.21−8.35 (bm, 12H, $H_{3,3'}$ and $H_{6,6'}$). **2** was too sensitive to give satisfactory elemental analysis data.

Preparation of [Mo(tmbp)$_3$] Complex (3). $MoCl_5$ (0.22 g, 0.8 mmol) was added to a solution of THF (30 mL) at −40 °C. After the resulting solution was warmed to room temperature, tmbp (0.49 g, 2 mmol) and magnesium powder (0.19 g, 8 mmol) were added. The reaction mixture was then stirred at 25 °C and monitored by ^{31}P NMR. After 1 h, ^{31}P NMR showed the unambiguous formation of **3**. After evaporation of THF, dichloromethane (50 mL) was added, and the resulting solution was filtered on Celite. The evaporation of dichloromethane yielded **3** as a deep-purple powder which was washed twice with hexane (2 × 10 mL) and then dried in vacuo. Yield: 0.28 g (50%). ^{31}P NMR ($CDCl_3$): δ 226.00. ^{1}H NMR ($CDCl_3$): δ 2.52 (bs, 18H, Me), 2.68 (bs, 18H, Me), 8.43 (bs, 6H, $H_{3,3'}$ or $H_{6,6'}$), 8.95 (bs, 6H, $H_{3,3'}$ or $H_{6,6'}$). Anal. Calcd for $C_{42}H_{48}P_6Mo$: C, 60.44; H, 5.80. Found: C, 60.40; H, 6.05.

Preparation of [W(tmbp)$_3$] Complex (4). [$WBr_4(MeCN)_2$] (1.43 g, 2.44 mmol) was added to a solution of THF at −20 °C. After the solution was warmed to room temperature, zinc dust (1.96 g, 30 mmol) and tmbp (1.5 g, 6.10 mmol) were added. The reaction mixture was then heated at 25 °C and monitored by ^{31}P NMR. After 1 h, a ^{31}P NMR control showed the completion of the reaction. After evaporation of THF, dichloromethane (80 mL) was added, and the resulting solution was filtered on Celite. The evaporation of dichloromethane yielded **4** as a deep-purple powder which was washed twice with hexane (2 × 25 mL) and then dried in vacuo. Yield: 1.22 g (65%). ^{31}P NMR ($CDCl_3$): δ 199.66, $^1J(^{31}P-^{183}W) = 291.16$ Hz). ^{1}H NMR ($CDCl_3$): δ 2.46 (bs, 18H, Me), 2.68 (bs, 18H, Me), 8.44 (bs, 6H, $H_{3,3'}$ or $H_{6,6'}$), 9.07 (bs, 6H, $H_{3,3'}$ or $H_{6,6'}$). UV/vis spectrum λ_{max} (±2) (nm) ($\epsilon \times 10^{-3}$ (M^{-1} cm^{-1})) in THF: 219 (50.2), 281 (72.5), 306 (41.3), 328 (44.9), 413 (21), 550 (21.5). Anal. Calcd for $C_{42}H_{48}P_6Mo$: C, 54.68; H, 5.24. Found: C, 54.62; H, 5.05.

X-ray Structure Determination for 4. The data set was collected on an Enraf Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. The crystal structure was solved by direct methods using SIR92[26] and refined with the Enraf Nonius MOLEN[27] package with reflections having $F^2 < 3.0\sigma(F^2)$. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. Crystal data are assembled in Table 1. The molecule contains a crystallographic 2-fold axis through the tungsten atom and the bridging C−C bond ($C_6-C_{6'}$) of one of the biphosphinine ligands. Despite the element of chirality, the compound crystallizes as a racemic in the space group *C*2/*c* (15).

Table 1. Crystal Data for Complex **4**[a]

formula	$C_{42}H_{48}P_6W{\cdot}C_4H_8O$
fw	994.65
space group	*C*2/*c* (15)
data collection temperature (K)	123
a (Å)	24.815(3)
b (Å)	14.700(2)
c (Å)	16.754(2)
β (deg)	127.57(1)
V (Å^3)	4844.5(2.5)
Z	4
d_{calc} (g/cm^3)	1.364
μ (cm^{-1})	26.6
maximum 2θ	60.0
no. of reflections measured	7527
reflections included	4973
parameters refined	267
unweighted agreement factor	0.029
weighted agreement factor	0.037
GOF	1.00
convergence, largest shift/error	0.01
minimization function	$w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, where $w = 4{*}F^2/\sigma^2(F^2)$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$, with $\sigma^2(F^2) = \sigma^2(I) + (pF^2)^2$

[a] $R_F = \sum(F_o - F_c)/\sum(F_o)$. $R_w = [\sum(w(F_o - F_c)^2)/\sum(wF_o^2)]^{1/2}$. GOF $= [\sum((w)(F_o - F_c)^2)/((\text{no. of rflns}) - (\text{no. of params}))]^{1/2}$.

Computational Details. The geometries were optimized by ab initio calculation within the framework of DFT(B3LYP) theory with the Gaussian94 package of programs.[16] The effective core potentials LANL2DZ were used for W, Mo, P, and S, and the valence electrons were represented by the associated double ζ quality basis set augmented by polarization functions for all atoms but the metal and hydrogen centers. The optimization was carried out with no symmetry restriction.

Acknowledgment. The authors thank the CNRS, the University of Cergy-Pontoise, the University of Montpellier 2, and the Ecole Polytechnique for supporting this work.

Supporting Information Available: X-ray structure determination for **4**, positional parameters and their estimated standard deviations, refined displacement parameters expressions β_{ij}, bond distances, and bond angles (4 pages). Ordering information is given on any current masthead page.

IC980042C

---

(26) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(27) Fair, C. K. *MolEN, An Interactive Intelligent System for Crystal Structure Analysis*, User Manual; Enraf−Nonius: Delft, The Netherlands, 1990.