EPR and DFT Studies of the Structure of Phosphinyl Radicals Complexed by a Pentacarbonyl Transition Metal

NDIAYE, Bassirou, et al.

Abstract

Paramagnetic complexes M(CO)\textsubscript{5}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}, with M = Cr, Mo, W, have been trapped in irradiated crystals of M(CO)\textsubscript{5}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{3} (M = Cr, Mo, W) and M(CO)\textsubscript{5}PH(C\textsubscript{6}H\textsubscript{5})\textsubscript{2} (M = Cr, W) and studied by EPR. The radiolytic scission of a P−C or a P−H bond, responsible for the formation of M(CO)\textsubscript{5}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}, is consistent with both the number of EPR sites and the crystal structures. The g and 31P hyperfine tensors measured for M(CO)\textsubscript{5}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2} present some of the characteristics expected for the diphenylphosphinyl radical. However, compared to Ph\textsubscript{2}P\textbullet{}, the 31P isotropic coupling is larger, the dipolar coupling is smaller, and for Mo and W compounds, the g-anisotropy is more pronounced. These properties are well predicted by DFT calculations. In the optimized structures of M(CO)\textsubscript{5}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2} (M = Cr, Mo, W), the unpaired electron is mainly confined in a phosphorus p-orbital, which conjugates with the metal dxz orbital. The trapped species can be described as a transition metal-coordinated phosphinyl radical.

Reference


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EPR and DFT Studies of the Structure of Phosphinyl Radicals Complexed by a Pentacarbonyl Transition Metal

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Paramagnetic complexes M(CO)₃P(C₆H₅)₂, with M = Cr, Mo, W, have been trapped in irradiated crystals of M(CO)₅P(C₆H₅)₂ (M = Cr, Mo, W) and M(CO)₅PH(C₆H₅)₂ (M = Cr, W) and studied by EPR. The radiolytic scission of a P–C or a P–H bond, responsible for the formation of M(CO)₅P(C₆H₅)₂, is consistent with both the number of EPR sites and the crystal structures. The g and ³¹P hyperfine tensors measured for M(CO)₅P-(C₆H₅)₂ present some of the characteristics expected for the diphenylphosphinyl radical. However, compared to Ph₂P⁺, the ³¹P isotropic coupling is larger, the dipolar coupling is smaller, and for Mo and W compounds, the g-anisotropy is more pronounced. These properties are well predicted by DFT calculations. In the optimized structures of M(CO)₅P(C₆H₅)₂ (M = Cr, Mo, W), the unpaired electron is mainly confined in a phosphorus p-orbital, which conjugates with the metal dₓz orbital. The trapped species can be described as a transition metal-coordinated phosphinyl radical.

1. Introduction

During the past five years many studies have invoked or confirmed the participation of metal-containing radicals to several mechanisms particularly important in modern chemistry. This is especially the case for metal-mediated oxygenation processes encountered in the synthesis of fine chemicals and in various areas of biochemistry (e.g., metalloenzymes).2,3 The crucial point in the description of an organometallic radical concerns the localization of the unpaired electron. In most cases, the chemical properties of the complex indicate that the transition metal contains 17 or 19 valence electrons, suggesting that the spin delocalization on the ligand is practically negligible. In some few cases (“Ligand Non-innocence”3), however, all the metal valence bond electrons remain paired, and the chemical behavior of the complex is similar to that of an organic radical.4–7 This type of structure has been reported for [R₃Ir-CH₂(CH₃)]⁺.8 In phosphorus chemistry several complexes have been reported in which the unpaired electron lies on the ligand; they generally result, however, from the reduction of a system containing an electron acceptor ligand, like a phosphinine or a phosphenium, able to stabilize the radical anion.9 In the present study, our purpose is to get information about the structure of system A composed of a neutral phosphorus-centered radical PR₃, a phosphinyl radical, bound to a transition metal moiety containing n d-electrons. Two other limiting structures can, a priori, be envisaged for such systems (Scheme 1).

SCHEME 1

In B, a phosphido-type ligand is linked to a metal containing (n – 1) d-electrons. Phosphido complexes are well documented,10 and their formation through the scission of the P–H bond of a complexed secondary phosphine has recently been used in the context of enantioselective catalysis.11 In C, the metal contains (n + 1) d-electrons while the ligand is formally a phosphonium group, a group 15 carbenoid. Structure and reactivity of carbenoids and phosphiniums continue to be objects of current interest12 as well as the chemistry of transition metal complexes containing a phosphonium ligand.13

Due to their reaction-intermediate nature, it is difficult to get information about the structure of transient metalated radicals. Liquid solution EPR is well suited to their identification but a part of the structural information is lost due to the averaging of the g and hyperfine tensors. There is no doubt that the most efficient method is to trap the metalated radical in an oriented matrix and to compare the resulting EPR tensors with those predicted by DFT calculations for the wanted species. The difficulty lies in the production of the transition metal-complexed radical. In the present study, we have tried to generate these species by exposing single crystals of phosphines complexed by metal pentacarbonyls to ionizing radiation. At room temperature, the diffusion of a group R resulting from the homolytic scission of a P–R bond is expected to be sufficiently efficient to lead to the trapping of M(CO)₃PR₂. The corresponding A structure (Scheme 1) is represented in Chart 1. In this work, EPR measurements and DFT calculations have been performed on complexes where the metal is Cr, Mo, or W and where the organic groups bound to the phosphorus atom are phenyl groups.

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† Department of Physical Chemistry.
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TABLE 1: Summary of Crystal Data, Intensity Measurement, and Structure Refinement

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<th>Cr(CO)₅P(C₆H₅)₃</th>
<th>Cr(CO)₅P(H)(C₆H₅)₂</th>
<th>W(CO)₅P(H)(C₆H₅)₂</th>
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<td>C₂H₁₅CrO₅P</td>
<td>C₆H₁₀O₅PW</td>
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<td>1.34(2)</td>
<td>1.78(2)</td>
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<td>0.035, 0.038</td>
<td>0.031, 0.020</td>
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</table>

ⁿ = 1/[σ(²(Fo) + p(Fo))], ᵇ S = [∑((Fo - Fc)²)/Nref]⁴, ᶜ R = [∑(|Fo| - |Fc|)/|Fo|] [∑|Fo|]⁴, ᵈ ωR = [∑(ω|Fo| - |Fc|²)/|Fo|²] [∑|Fo|²]⁴.

2. Experimental Section

Compounds. Syntheses of Cr(CO)₅P(C₆H₅)₃, Mo(CO)₅P-(C₆H₅)₃, and Mo(CO)₅P(C₆H₅)₂ have been published.¹⁴ The syntheses of Cr(CO)₅P(H)(C₆H₅)₂ and W(CO)₅P(H)(C₆H₅)₂ have been carried out by adapting the method reported by Mathey et al. for W(CO)₅P(C₆H₅)₂.¹⁵

Crystal Structure. A Summary of crystal data, intensity measurement, and structure refinement is reported in Table 1. For each crystal structure, hydrogen atoms were observed and refined with a fixed value of their isotropic displacement parameters. CCDC 600424 to 600426 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+ 44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Single-Crystal EPR Measurements. EPR spectra were recorded on a Bruker spectrometer (X-band). The angular variations of the EPR signals were recorded in the three reference planes of a Cartesian referential XYZ oriented with respect to the crystallographic axes as follows: for Cr(CO)₅P-(C₆H₅)₃ X/a, Y/b, Z/c; for Cr(CO)₅P(H)(C₆H₅)₂ X/a*, Y/b, Z/c; for Mo(CO)₅P(C₆H₅)₃ X/a*, Y/c*, and Z/b for W(CO)₅P(C₆H₅)₂ X/b*, Y/b, and Z/a; for Cr(CO)₅P(H)(C₆H₅)₂ X/c*, Y/b, Z/a. The EPR tensors were determined by using an optimization program that compares the positions of the signals with the resonance field positions calculated by using second-order perturbation theory.¹⁶ The angular variations of the EPR signals obtained with the five crystals are given in the Supporting Information.

Calculations. DFT calculations were performed with the Gaussian 03 package.¹⁷ All the geometries were optimized by using the hybrid functional B3LYP.¹⁸,¹⁹ the standard 6-31G-(d,p) basis set for H, C, O, and P, and the basis set SBKJC²⁰,²¹ developed by Stevens et al. for the transition metal. The SBKJC set²³ uses Relativistic Compact Effective Potentials and efficient, share-exponent basis sets for the third-, fourth-, and fifth-row atoms. In this approach, outermost (n + 1)s orbitals (where n is the principal quantum number), the partially occupied nd orbitals, as well as the ns and np orbitals are considered to be part of the valence space. For transition metals the basis functions consist of double-ζ quality sp basis sets (contraction 4,1) and triple-ζ d basis sets (contraction 4,1,1 for third row; 3,1,1 for fourth and fifth rows), and the outer s and p primitives are contracted 2,1 for Cr and Mo and 1,1 for W. Two sets of calculations were performed for the prediction of the g and hyperfine tensors. The first one used the IGLO-III basis set²² Invainant Gauge Localized Orbitals) for H, C, O, and P atoms while the second one used the TZVP basis set.²³ In IGLO-III, the Gaussian-type functions, developed by Kutzelnig and intended for computing magnetic properties, were derived from Double-ζ Huzinaga functions to which a double set of polarization functions was added. This basis set consists of the following contractions: (6s,2p)[4s,2p] for H, (11s,7p,2d)[7s,6p,2d] for first-row atoms, and (12s,8p,3d)[8s,7p,3d] for second-row atoms. The TZVP basis set²¹,²³ consists of the contractions (5s,1p)[3s,1p] for H, (10s,6p,1d)[4s,3p,1d] for C and O, and (13s,9p,1d)[5s,4p,1d] for P.

Minima were characterized with harmonic frequency calculations (no imaginary frequencies). Molecular orbitals were represented using the GaussView program.²⁴

Many studies have been devoted to the calculation of EPR properties.²⁵ The isotropic part (Fermi contact interaction) and
the anisotropic part (electron–nuclear dipole interaction) of the hyperfine interaction at a nucleus N can be expressed as

\[ A_{\text{iso}} = (8\pi/3)g\beta g_N \delta_{\text{iso}} \sum_{ij} \langle \mu \nu | \rho_{ij} | \delta_i \rangle \phi_j \]

\[ g_{pq}^N = -g\beta g_N \delta_{\text{iso}} \sum_{ij} \langle \mu \nu | \rho_{ij} | (r^2 \delta_{pq} - 3pq) r^{-5} \rangle \phi_j \]

respectively. The molecular orbitals are defined as linear combinations of atomic orbitals \( \phi_A \), \( \rho_{ij} \) represents an element of the one-electron spin density matrix, and \( pq \) the spatial coordinates \( x,y,z \) relative to the nucleus N.

Calculation of the elements of the g-tensor requires evaluating four contributions:\textsuperscript{26}

\[ g_{rs} = e_\alpha \delta_{rs} + \Delta g_{\text{RMCT}} \delta_{rs} + \Delta g_{\text{iso(GC)}} + \Delta g_{\text{iso(OZ/SOC)}} \]

The first term corresponds to the value of the free electron; the second one is due to the relativistic mass correction to the kinetic energy. The diamagnetic correction \( \Delta g_{\text{GC}} \) involves the effective spin–orbit coupling interaction \( \xi(A,i) \) of the electron i at the nucleus A (with \( \xi(r_{AA}) = \alpha Z^2 r_{AA}^2 (r_i - r_A)^3 \)), where \( Z_{\text{eff}} \) is an effective nuclear charge for atom A at position \( r_{AA} \). \( \Delta g_{\text{iso(OZ/SOC)}} \) arises as a cross term between the orbital Zeeman \( (H_{\text{SOZ}} = \beta Z_{\text{eff}}) \) li(i) and spin–orbit coupling \( (H_{\text{SOC}} = \sum \xi(r_A)\alpha_A l_A s(i)) \) operators. \( l(i) \) is the angular momentum operator of the ith electron relative to the chosen gauge origin and \( s(i) \) is the spin operator for this electron.

3. Results

3.1. Crystal Structures. The crystal structures of three of the five diamagnetic precursors, \( \text{M(CO)}_5 \text{P(C}_6 \text{H}_5)_3 \), \( \text{M = Mo, W, Cr} \), and \( \text{Cr, Mo, W} \) are isostructural and are available in the literature.\textsuperscript{30} However, for \( \text{M = Cr} \), the crystals used in our EPR study were found to grow in another crystal system; the corresponding structure is reported below. Both structures of isostructural compounds \( \text{Cr(CO)}_5 \text{P(H)(C}_6 \text{H}_5)_2 \) and \( \text{W(CO)}_5 \text{P(H)(C}_6 \text{H}_5)_2 \) were also determined in the present study. An ORTEP view of the crystal structure of \( \text{Cr(CO)}_5 \text{P(H)(C}_6 \text{H}_5)_2 \) is given in Figure 1.

The principal geometrical parameters determined from the crystal structures are given in Table 2. The five complexes adopt the classical square-planar bipyramid structure with a \( \text{M–C}_{\text{axial}} \) distance slightly shorter than the \( \text{M–C}_{\text{equatorial}} \) bond lengths. The \( \xi \) angles formed by the normal to the RPR planes and the \( \text{M–P} \) bond indicate that the coordination of the phosphorus atom is not too far from tetrahedral (for a pure tetrahedron \( \xi = 35.26^\circ \)). As shown by the sum of the CPC (and CPH) angles, which is between 300° and 309°, the pyramidality of the phosphine moiety is not very affected by the coordination to the metal atom (for the isolated triphenylphosphine \( \Sigma R_{\text{P}}, P_{\text{R}} = 308.9^\circ \)).

3.2. EPR Measurements. The spectra obtained at room temperature with the five irradiated crystals presented all the same features: an anisotropic coupling with a spin \( \frac{1}{2} \) nucleus—certainly \( \text{P} \)—and a rather pronounced g anisotropy. An example of a spectrum obtained with a crystal of \( \text{Cr(CO)}_5 \text{P(C}_6 \text{H}_5)_3 \) is shown in Figure 2 (signals R).

The EPR tensors determined after analysis of the angular dependences\textsuperscript{32} are shown in Table 3 together with the values previously reported for the isolated \( \text{P(C}_6 \text{H}_5)_3 \) radical.\textsuperscript{33}

For all species, the symmetry of the \( \text{P} \) hyperfine tensor is axial (with the largest eigenvalue \( T_{\text{max}} = T_0 \) and \( g_{\text{min}} \) close to the free electron value), is oriented in the vicinity of the \( \text{P} \)–T\text{III} vector. Moreover, as shown in Table 4, decomposition into isotropic and anisotropic \( \text{P} \)-coupling constants clearly indicates that a large amount of the unpaired electron resides in a phosphorus p-orbital. Comparison with atomic hyperfine constants\textsuperscript{34} leads to a crude estimation of the s and p characters of the spin-containing phosphorus orbital \( \rho_s \approx 0.035 \) and \( \rho_p \approx 0.55 \). These properties are similar to those expected for a phosphinyl radical\textsuperscript{33} and suggest a homolysis scission of a phosphine bond. We will therefore examine if this interpretation is consistent with the properties of the crystals.

After rupture of a \( \text{P–C} \) bond in \( \text{M(CO)}_5 \text{P(C}_6 \text{H}_5)_3 \), the resulting radical relaxes to its minimum energy conformation; this process is likely to be hindered by the environment of the remaining phenyl rings. As shown by the crystal structure, in each compound the environments of the three phenyl rings are slightly different. This is clearly seen from the three different \( \xi \) values measured in each complex (Table 2) and from the \( \text{P–C} \) phenyl bonds which are differently oriented with regard to the metal–carbon bonds of the equatorial plane. For example, in \( \text{Mo(CO)}_5 \text{P(C}_6 \text{H}_5)_3 \) (where C1, C2, C3, and C4 form the equatorial plane), the \( \text{P–C} \) bond lies in the C3–Mo–C4 bisector while the bonds \( \text{P–C6} \) and \( \text{P–C7} \) make dihedral angles of 15° with Mo–C1 and Mo–C2, respectively. Due to these differences in the orientations of the phenyl rings, the final structure of the trapped radical is expected to be slightly dependent upon which of the three \( \text{P–C} \) bonds has been broken.
This explains the three sets of tensors obtained for Mo(CO)₅P(C₆H₅)₃ and for W(CO)₅P(C₆H₅)₃. For Cr(CO)₅P(C₆H₅)₃, curiously, only one P-C bond undergoes a homolytic scission such a selection in the bond cleavage is tentatively attributed to crystal packing. For Cr(CO)₅P(H)(C₆H₅)₂ and W(CO)₅P(H)(C₆H₅), the favored diffusion of a hydrogen atom leads to the cleavage of the P-H bond only; the two orientations observed for the trapped radical are merely due to the monoclinic symmetry of the crystal.

3.3. DFT Calculations. 3.3.1. Diphenylphosphinyl Radical. Preliminary calculations were devoted to the structure of the phosphinyl radical Ph₂P\(^¥\). Its geometry was optimized and the \( g \) and \( ^{31}P \) hyperfine tensors were calculated. These tensors will be reported in Table 6. A representation of the SOMO of Ph₂P\(^¥\) is shown in Figure 3.

As expected, the unpaired electron is localized in a phosphorus p-orbital oriented perpendicular to the RPR plane. The \( g_{\text{min}} \) and \( ^{31}P-T_{\|} \) components are aligned along this orbital direction. The normals to the phenyl rings form an angle of 51°.

3.3.2. Complexed Phosphinyl Radicals. The optimized parameters of complexed phosphinyl radicals are reported in Table 5. The \( ^{31}P \) isotropic and anisotropic coupling constants as well as the \( g \)-tensors calculated for the various metalated phosphinyl species are reported in Table 6, together with the corresponding values calculated for the isolated P(C₆H₅)₂ radical. The IGLO-III and TZVP basis sets lead to rather similar values.

4. Discussion

Although the EPR tensors of the paramagnetic species trapped in the crystal matrices of pentacarbonylmetal complexes (see Tables 3 and 4) present several similarities with those expected for a phosphinyl radical (e.g., axiality of the \( g \) and \( ^{31}P \) hyperfine tensors, relative orientation of these tensors), these tensors differ...
from those measured for isolated \( \text{Ph}_2 \text{P}^+ \) radicals by at least two features: (1) the \( ^{31}\text{P} \) isotropic coupling constants are almost twice as large as those for \( \text{Ph}_2 \text{P}^+ \), whereas the anisotropic coupling constants are appreciably smaller than those for the phosphinyl radical, and (2) the \( g \) anisotropy is more marked for the Mo and W complexes than for the isolated radical. Since the properties calculated for \( \text{M(CO)}_5 \text{PR}^2 \) (Table 6) are well-known to accurately determine the dipolar hyperfine interactions. For almost all complexed radicals reported in Tables 4 and 6, the measured and calculated \( ^{31}\text{P} \) anisotropic coupling tensors present an axial symmetry and, taking a small dispersion of the experimental values due to the various environments (vide supra) into account, the accord between experimental and DFT values for the \( \xi \) component is excellent. As often reported for phosphorus radicals, the predicted isotropic \( ^{31}\text{P} \) couplings are noticeably smaller than the experimental ones; nevertheless, it is worthwhile remarking that DFT predicts an increase of between 50% and 100% when passing from \( \text{P(} \text{C}_6 \text{H}_5 \text{)}_2 \) to \( \text{P(CO)}_5 \text{P(} \text{C}_6 \text{H}_5 \text{)}_2 \) and that this change is consistent with the increase measured on the EPR spectra.

Finally, the \( g \)-eigenvalues calculated for \( \text{M(CO)}_5 \text{PPh}_2 \) (\( \text{M} = \text{Cr}, \text{Mo}, \text{W} \)) reasonably agree with the experimental values reported in Table 3, inasmuch as the relative orientations of the \( g \) and \( ^{31}\text{P} \) hyperfine coupling correspond to the orientation determined from EPR measurements. The calculated \( g \)-tensors confirm that coordination of \( \text{PPh}_2 \) to \( \text{Mo(CO)}_5 \) and \( \text{W(CO)}_5 \) provokes an appreciable enhancement of the \( g \) anisotropy.

Since the properties calculated for \( \text{M(CO)}_5 \text{PR}^2 \) (Table 6) are consistent with those measured by EPR, we can use DFT to describe the structure of complexed phosphinyl radicals. This structure is illustrated for \( \text{Mo(CO)}_5 \text{P(} \text{C}_6 \text{H}_5 \text{)}_2 \) in Figure 4; the reference axes are defined in Figure 5. The lone pair of the \( \text{sp}^2 \)-hybridized phosphorus atom forms a \( \sigma \) bond with the empty metal \( d_z^\text{e} \) orbital. The antibonding combination resulting from the interaction between the \( p_z \) phosphorus orbital oriented perpendicular to the CPC plane and the doubly occupied molybdenum \( d_z^\text{c} \) orbital leads to the SOMO shown in Figure 4.

This SOMO corresponds, in fact, to the LUMO of the phosphinidene transition metal complex described by Nguyen.\textsuperscript{35} We have optimized the structure of the phosphinidene \( \text{Mo(CO)}_5 \) complex with the functional and basis sets used for the

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**Figure 4.** (a) SOMO for \( \text{Mo(CO)}_5 \text{P(} \text{C}_6 \text{H}_5 \text{)}_2 \) and (b) LUMO for \( \text{Mo(CO)}_5 \text{P(} \text{C}_6 \text{H}_5 \text{)}_2 \).
phosphinyl Mo(CO)₅ complex. The resulting LUMO is shown in Figure 4. By passing from the phosphinidene complex M(CO)₅PR (singlet state) to M(CO)₅PR₂, one of the phosphorus lone pairs is replaced by a σ P–C bond and an unpaired electron occupies the vacant πₚ orbital. For the three complexes M(CO)₅P(C₆H₅)₃ (M: Cr, Mo, W), the C–P–C bond angle is equal to ca. 107° and the P–M bond lies in the bisector of this angle. For both the molybdenum and the tungsten complexes, the ξ angle formed by the P–M bond and the normal to the two P–R bonds (Table 5) is equal to 90°, indicating that the CPC plane is perpendicular to the equatorial plane. Such a structure readily explains the differences in the EPR parameters that accompany the coordination of the diphenylphosphinyl radical to the molybdenum pentacarbonyl moiety.

The overlap between the phosphorus πₚ orbital and the metal dₓz orbital delocalizes a small part of the spin onto the metal. This tends to enhance the g anisotropy and appreciably changes the 31P hyperfine interaction: decrease in the dipolar coupling (from 519 MHz for P(C₆H₅)₂ to 453 MHz for Mo(CO)₅P-(C₆H₅)₂) due to a diminution of the phosphorus p spin density and increase in the isotropic coupling Aiso (from 164 MHz to 281 MHz). This enhancement of Aiso is probably due to the presence of spin in the dₓz orbital, which polarizes the metal—phosphorus σ bond. Such a polarization, even though quite small, is expected to increase the Fermi interaction at the phosphorus nucleus since the corresponding σ orbital has a pronounced s character (formally a phosphorus sp² orbital).

This interpretation is also consistent with the results obtained for the chromium complex although, in this case, the metal atom does not exactly lie in the PCP plane.

It is worthwhile remarking that, as indicated by the experimental (Table 4) and calculated (Table 6) values, the phosphorus spin density for M(CO)₅P(C₆H₅)₃ hardly varies when going down in column 6 of the Periodic Table while the g anisotropy appreciably increases. This g variation is therefore mainly caused by an increase of the spin–orbit coupling constant. 36

5. Conclusion

As confirmed by DFT calculations, complexes between phosphinyl radicals and transition metal pentacarbonyls could be stabilized, at room temperature, in crystalline matrices. They show that in M(CO)₅P(C₆H₅)₃ the unpaired electron mainly resides in a phosphorus p orbital, which is oriented parallel to the equatorial plane of the complex. The interaction between this orbital and a dₓz metal orbital leads to appreciable changes in the 31P coupling tensors as compared to those measured or calculated on the isolated phosphinyl species. For the Mo and W complexes an increase in the g anisotropy is also detected. The mechanism used to rationalize these changes implies a small delocalization of the spin from the phosphorus p orbital to the metal dₓz orbital. Nevertheless, the main characteristics of the phosphinyl radicals are maintained, in accordance with structure A of Scheme 1 and a very small contribution of structure C.

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Supporting Information Available: Experimental angular variations of the EPR spectra in the three reference planes for Cr(CO)₃P(C₆H₅)₃, Cr(CO)₃P(H)(C₆H₅), Mo(CO)₅P(C₆H₅), W(CO)₅P(C₆H₅)₃ and W(CO)₅P(H)(C₆H₅)₂ together with the angular dependences calculated with the tensors given in Table 2, optimized structures for (C₆H₅)₂P⁺ figures showing atom numbering and ellipsoids for the crystal structures, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(3) The adjective “non-innocent” was first used by C. K. Jorgensen for ligands where the degree of electron donation is uncertain due to their σ-acceptor character. Jorgensen, C. K. Oxidation numbers and oxidation states; Springer: Berlin, Germany, 1969.

(21) Basis set obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352.

(22) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In NMR—Basic Principles and Progress; Springer-Verlag: Heidelberg, Germany, 1990; Vol. 23.


(24) GaussView 3.0; Gaussian, Inc.: Pittsburgh, PA.


(30) It should be noted that for M = Mo27 and Cr,29 the published unit cells were not reduced. All EPR reference axes reported in the present article were defined from the reduced cells (a < b < c and α, β, γ < 90°).


(32) The angular variations of the EPR spectra, in the three reference planes, for the five single crystals Cr(CO)3P(C6H5)3, Cr(CO)3P(H)(C6H5)2, Mo(CO)3P(C6H5)3, W(CO)3P(C6H5)3, and W(CO)3P(H)(C6H5)2 are given as the Supporting Information.


(36) Some spin−orbit coupling constants (e.g., for Cr(I) 56 cm−1, for Mo(I) 168 cm−1, for W(I) 607 cm−1) are compiled in: Fraga, S.; Karwowski, J.; Saxena, K. M. S. Handbook of atomic data; Elsevier: New York, 1976.