

Chromium tricarbonyl complex of phosphalkene: Crystal structure and electrochemistry of the $\text{Cr}(\text{CO})_3$ complex of $\text{PhC}(\text{H})=\text{PMes}^*$, EPR and DFT studies of its radical anion

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Abstract

We report the synthesis, crystal structure and electrochemical behaviour of a complex in which the Ph group of the phosphalkene $\text{PhC}(\text{H})=\text{PMes}^*$ (Mes^* : 2,4,6-tri-*tert*-butylphenyl) is coordinated to a chromium tricarbonyl group. The EPR spectra resulting from electrochemical and chemical reductions are described and the experimental g and hyperfine tensors (^{31}P)T, as determined from the EPR data, are compared with those predicted by DFT calculations for the radical anion $(\text{Cr}(\text{CO})_3, \text{PhC}(\text{H})=\text{PMes}^*)^-$. The structural changes caused by the addition of an electron to the neutral complex are described, together with an estimation of the contribution of $\text{Cr}(\text{CO})_3$ to the stabilization of the radical anion.

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1. Introduction

Phosphalkenes (e.g. **1'**) are well known for their ability to accept an extra electron in their π^* orbital [1–4]; some systems containing a $\text{P}=\text{C}$ bond have already been investigated for their potential applications in molecular electronics [5]. However, the reduction potentials of phosphalkenes are rather low ($E_o = -1980$ mV/SCE for **1'**) and the stability of their radical anion remains modest. Therefore, it is desirable to modify their electronic structure to facilitate the reduction process and to increase the stability of the resulting radical anion. One approach is to directly coordinate the phosphorus atoms of two phosphalkene moieties to a transition metal in a chelating structure. This method, which was successfully used some years ago, requires the rather delicate synthesis of pincer type ligands [6]. Another easier approach is to take advantage of the presence of a transition

metal in the vicinity of the phosphalkene moiety. To this purpose, the properties of tricarbonylchromium group seem, a priori, well suited. Indeed, $\text{Cr}(\text{CO})_3$, referred to as a “hermaphrodite” group, has been shown to produce stabilization of both benzylic anions and cations [7–9]. In the present study, we report the synthesis and crystal structure of a phosphalkene complex, in which the phenyl ring bound to the phosphalkenic carbon is coordinated to $\text{Cr}(\text{CO})_3$. The electron-acceptor properties of this system (**1**) are studied by cyclic voltammetry and EPR spectroscopy. Experimental hyperfine couplings and DFT calculations are used to assess the structural modifications that accompany the one-electron reduction of **1**.

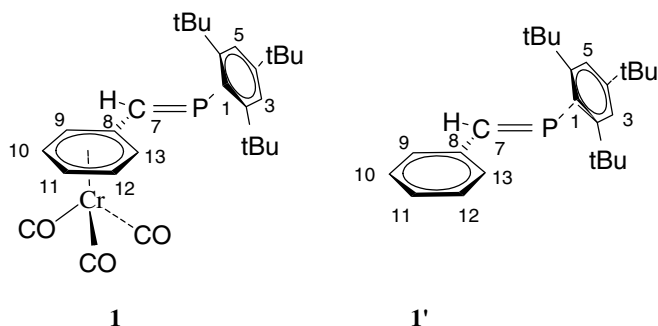
2. Experimental

2.1. Analytical instrumentation

^1H , ^{13}C and ^{31}P NMR spectra were recorded on a Bruker 400 or 500-MHz, and Varian-XL 200 spectrometers. High-resolution mass spectra (HR-MS) were measured

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on a VG analytical 7070E instrument (data system 11250, resolution 7000).



2.2. Syntheses

All manipulations involving organometallics were carried out under an atmosphere of purified nitrogen and with an inert-gas-vacuum double manifold and standard Schlenk technique. $\text{Cr}(\text{CO})_6$ was supplied by FLUKA and used as received. Tetrahydrofuran, diethyl ether, and dibutyl ether were distilled from sodium-benzophenone ketyl immediately before use. Hexane was distilled from metallic sodium. *n*-BuLi (FLUKA) was titrated before use according to the method of Chong [10]. Mes^*PH_2 [11,12] and tricarbonyl [1,2,3,4,5,6- η -benzaldehyde]chromium [13,14] were synthesized following methods described in the literature. The synthesis of the ^{13}C -enriched compound was performed using ^{13}C -labelled benzaldehyde supplied by Cambridge Isotope Labs. Column chromatography was carried out by using the flash method described by Still [15]. All other reagents were commercial.

Early studies on reaction of low-coordinated organo-phosphorus systems with chromium(0) carbonyls have shown that diaryldiphosphenes complex tricarbonylchromium via their benzene ring [16,17], whereas **1'** forms a phosphorus-coordinated complex with $\text{Cr}(\text{CO})_5$ [18]. In the present work, we could synthesize **1** by reacting Mes^*PH_2 with tricarbonyl [1,2,3,4,5,6- η -benzaldehyde]chromium. 3.4 mL of *n*-BuLi (1.6 M in hexane, 5.4 mmol) was added dropwise at -78°C to a carefully degassed solution of 1.5 g of Mes^*PH_2 (5.4 mmol) in 12 mL of THF. After 5 min, the solution was allowed to warm to room temperature and stirred for another 15 min. After addition of 0.815 g of *t*-BuMe₂SiCl (5.4 mmol) the reaction mixture was stirred for 30 min. Thereafter, 3.4 mL of *n*-BuLi (1.6 M in hexane) was added at -78°C while stirring vigorously. After warming to room temperature, 1.83 g (7.5 mmol) of tricarbonyl [1,2,3,4,5,6- η -benzaldehyde]chromium was added to the solution which was stirred overnight. The solvents were removed under vacuum, and the resulting brown residue was purified by column chromatography on SiO_2 using hexane as an eluant. This yielded 1.2 g of an orange powder (yield = 44%). Red crystals were obtained after recrystallisation from Et₂O. M.p. 155–157 °C.

The ^{13}C -enriched compound $\text{Cr}(\text{CO})_3$, Ph $^{13}\text{C}(\text{H})=\text{PMes}^*$ was obtained by following the same procedure and by

using $\text{C}_6\text{H}_5\text{-}^{13}\text{C}(\text{H})\text{O}$ for the synthesis of tricarbonyl [1,2,3,4,5,6- η -benzaldehyde]chromium.

$^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, C_6D_6): $\delta = 266.04$ (d, $J_{\text{PH}} = 24.0$ Hz). ^1H NMR (500 MHz, C_6D_6): 1.37 (s, 9H, $\text{C}_{\text{para}}\text{-CMe}_3$), 1.62 (s, 18H, $\text{C}_{\text{ortho}}\text{-CMe}_3$), 4.29 (t, 2H, $J = 6.2$ Hz, H_{arom}), 4.51 (t, 2H, $J = 6.2$ Hz, H_{arom}), 5.11 (d, 2H, $J = 6.2$ Hz, H_{arom}), 7.35 (d, 1H, $^2J_{\text{PH}} = 24.2$ Hz $\text{P}=\text{C}-\text{H}$), 7.65 (s, 2H, H_{arom}). ^{13}C NMR (spectra recorded with the ^{13}C enriched compound, 125 MHz, C_6D_6): $\delta = 31.44$ (s, $\text{C}_{\text{para}}\text{-CMe}_3$), 34.10 (s, $\text{C}_{\text{ortho}}\text{-CMe}_3$), 35.08 (s, $\text{C}_{\text{para}}\text{-CMe}_3$), 38.44 (s, $\text{C}_{\text{ortho}}\text{-CMe}_3$), 89.99 (s, C_{arom}), 92.32 (s, C_{arom}), 92.47 (s, C_{arom}), 93.49 (s, C_{arom}), 122.24 (s, C_{meta}), 137.66 (d, $J_{\text{PC}} = 52.5$ Hz, $\text{C}_{\text{ipso}}\text{-P}$), 150.62 (s, C_{para}), 154.95 (s, C_{ortho}), 171.28 (d, $^1J_{\text{PC}} = 35.8$ Hz, $\text{C}=\text{P}$), 233.20 (s, $\text{C}=\text{O}$). HR-MS: calculated for $^{12}\text{C}_{28}\text{-}^1\text{H}_{35}\text{-}^{31}\text{P}\text{-}^{16}\text{O}_3\text{-}^{52}\text{Cr}^+$ 502.17289, measured 502.17390.

2.3. Crystal structure determination

Red needles of **1** suitable for X-ray analysis were obtained by slow evaporation of a solution in diethyl ether. Cell dimensions and intensities were measured at 200 K on a STOE IPDS diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz polarization effects and for absorption. A summary of crystal data, intensity measurement and structure refinement is reported in Table 1. The structure

Table 1

Summary of crystal data, intensity measurement and structure refinement for compound **1**

Formula	$\text{C}_{28}\text{H}_{35}\text{CrO}_3\text{P}$
Molecular weight	502.6
Crystal Size (mm)	$0.057 \times 0.185 \times 0.35$
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> (Å)	5.9621(3)
<i>b</i> (Å)	26.5621(10)
<i>c</i> (Å)	16.8347(10)
β (°)	96.729(7)
<i>V</i> (Å ³)	2647.7(3)
<i>Z</i>	4
D_{calc} (g cm ⁻³)	1.261
μ (Mo $\text{K}\alpha$) (mm ⁻¹)	0.518
$T_{\text{min}}, T_{\text{max}}$	0.8971, 0.9705
$((\sin\theta)/\lambda)_{\text{max}}$ (Å ⁻¹)	0.637
<i>N</i> (measured)	25704
<i>N</i> (independent)	5535
<i>N</i> (observed)	3124
Criterion for observed	$ F_o > 4\sigma(F_o)$
Refinement (on <i>F</i>)	Full-matrix
<i>N</i> (parameters)	298
Weighting scheme p^a	0.0001
Maximum Δ/σ	0.0013
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ (e Å ⁻³)	0.424, -0.327
S^b (all data)	1.49(2)
$R^c, \omega R^d$	0.033, 0.032

^a $\omega = 1/[\sigma^2(F_o) + p(F_o)^2]$.

^b $S = [\sum\{((F_o - F_c)/\sigma(F_o))^2\}/(N_{\text{ref}} - N_{\text{var}})]^{1/2}$.

^c $R = \sum|F_o| - |F_c|/\sum|F_o|$.

^d $\omega R = [\sum(\omega|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2}$.

was solved by direct methods (SIR-97) [19]; all other calculations were performed with the XTAL [20] system.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-277168. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or deposit@ccdc.cam.ac.uk].

The crystal structure of the non-complexed phosphalkene **1'** was first reported by Appel et al. [21]. The structures of the *E* and *Z* isomers of **1'** were discussed by Yoshifujii et al. [22].

2.4. Electrochemistry

Cyclic voltammetry measurements were performed on a BAS station (model CV-50W). A standard three-electrode cell was used, with positive feedback IR compensation. All measurements were carried out under dry argon. The solvent was THF, dried in a glove box over activated 4 Å molecular sieves, the supporting electrolyte was *n*-Bu₄PF₆ (0.1 M), twice recrystallized and melt-dried under vacuum. The electrodes were 1 mm diameter platinum wire as working and counter-electrode, and a SCE reference electrode. The standard potential of ferrocene in THF is equal to 575 mV in our experimental conditions.

2.5. EPR spectroscopy

Spectra were recorded on a Bruker 200D spectrometer (X-band, 100 kHz field modulation) with a Bruker ER-4111 VT variable temperature controller. Samples were usually prepared by electrolysis in situ of a thoroughly argon-degassed solution of the compound. A two-platinum electrodes cell was used, adjusting the voltage until a signal appeared.

2.6. Computations

All the computations, including the geometry optimizations, were carried out with the GAUSSIAN 03 set of programs [23], using the B3LYP functional (Becke's three-parameter nonlocal exchange potential [24] coupled to the nonlocal correlation functional of Lee, Yang and Parr [25]) combined with several basis sets. The following designations for the basis sets are used throughout the text for negatively charged species: (1) 6-31+G* for all atoms (basis set 1), (2) LANL2DZ [26] for Cr and, for the other atoms, either 6-31+G* (basis set 2), IGLO3 [27] (basis set 3) or TZVP [28] (basis set 4). The same designations are used for neutral species, except that the 6-31+G* basis set is replaced by the 6-31G* set. Minima on potential energy surfaces were characterized with harmonic frequency calculations (no imaginary frequencies). The stabilization energy (homodestic reaction *a*, vide infra) was performed by calculating, with the 6-31+G* basis set, the energy of

all reactants and products at their geometry optimized with basis set 2. Molecular orbital visualisations were performed using the MOLEKEL program [29].

3. Results

3.1. Crystal structure

An ORTEP representation of **1** is given in Fig. 1. The phosphalkene part of the complex adopts an *E* conformation and is hardly affected by the presence of Cr(CO)₃: The P=C bond length = 1.666(3) Å (1.674 Å in **1'**), the C1,P,C7,C8 atoms lie in the same plane (torsion angle C1–P–C7–C8 = –177.3(2)° (177.8° in **1'**) oriented perpendicular to the Mes* phenyl ring (torsion angle C7–P–C1–C6 = –87.7(2)°). The complexed phenyl ring remains planar. The presence of the Cr(CO)₃ group causes an appreciable rotation of this phenyl ring around the C7–C8 bond (P–C7–C8–C9 torsion angle = 25.4(3)° in **1** and 16.0° in **1'**) as well as a small increase in the C7–C8 bond length (1.477(3) Å in **1**, 1.456 Å in **1'**). The Cr–C_{phenyl} distances lie in the range 2.197 Å (Cr–C13) to 2.237 Å (Cr–C8).

3.2. Electrochemistry

At room temperature, cyclic voltammetry of a solution of **1** in THF shows a quasi-reversible one-electron reduction at the platinum electrode (Fig. 2). The anodic and cathodic peak potential values are $E_p(a) = -1456.5$ mV and $E_p(c) = -1643.5$ mV vs. SCE, respectively ($E_{1/2} = -1554.5$ mV vs. SCE, $\Delta = 187$ mV). $I_p(a) = I_p(b)$.

3.3. EPR

An example of EPR spectrum obtained at 290 K after reaction at the same temperature of a solution of **1** in THF on a potassium mirror is shown in Fig. 3(a). This spectrum is characterized by a ³¹P isotropic coupling of 217 MHz and by a *g*-value equal to 2.0049. In the frozen solution, at 110 K, the spectrum spreads over more than

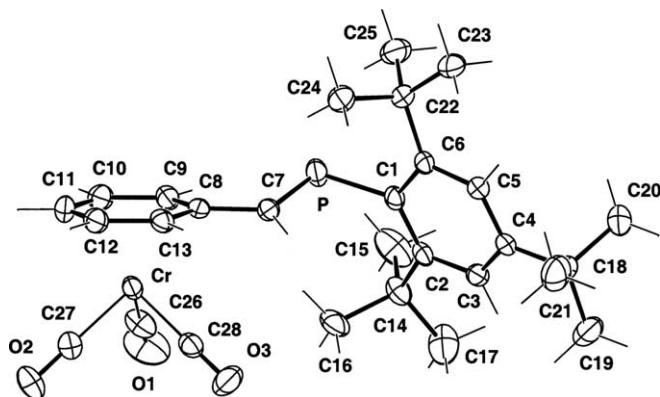


Fig. 1. ORTEP view of **1** with atom numbering. Ellipsoids are represented with 50% probability level.

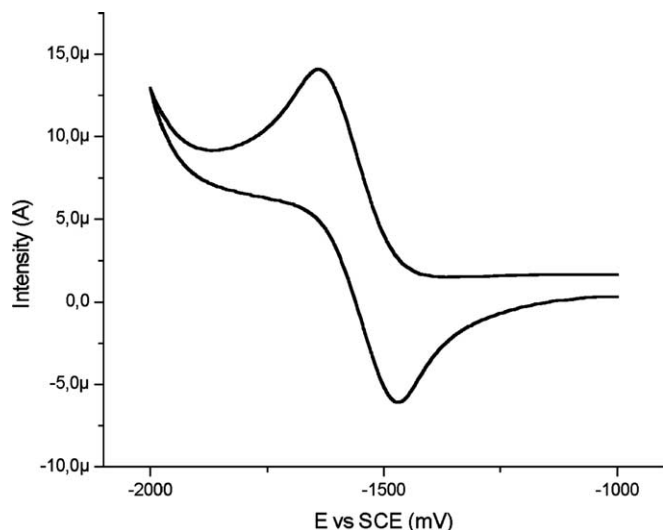


Fig. 2. Cyclic voltammogram of **1**.

200 G (Fig. 3(b)) showing a large anisotropy of the ^{31}P hyperfine interaction. This spectrum is well simulated by using the axial g and hyperfine (^{31}P) \mathbf{T} tensors given in Table 1. The isotropic ^{31}P coupling constant (221 MHz) and the average g -value (2.0045) obtained from the spectrum of the frozen solution agree well with the values obtained at 290 K. The same spectra were obtained by reducing a THF solution of **1** with sodium naphthalenide or by direct electrolysis of this solution, in situ, in the EPR cavity.

The isotropic and anisotropic coupling constants $\tau(^{31}\text{P})$, deduced from the $\mathbf{T}(^{31}\text{P})$ coupling tensor, are reported in Table 2. The experimental spin densities can be obtained by comparing these values with the Fermi contact and dipolar interactions characterizing an unpaired electron located in a 3s and 3p orbital of atomic phosphorus, respectively [30]. The resulting $\rho_s(\text{P})$ and $\rho_p(\text{P})$ are given in Table 2. No modification of the spectrum could be detected as compared to **1**, when the ^{13}C enriched complex $\text{Cr}(\text{CO})_3$, $\text{C}_6\text{H}_5^{13}\text{C}(\text{H})=\text{PMes}^*$ was used instead for the in situ reduction.

3.4. DFT calculations

Due to the large size of **1**, the DFT calculations were carried out on model systems **1a**, in which the cumbersome Mes* group was replaced by a mesityl group. The various basis sets (vide supra) lead to very similar optimized geometries for this complex. A representation of the optimized structure (B3LYP/ basis set 2) for the neutral complex **1a** is given in Fig. 4. The corresponding geometrical parameters, together with those obtained from the optimization of the non-complexed phosphalkene $\text{PhC}(\text{H})=\text{PMes}$ (**1'a**) [31], are given in Table 3.

Taking into account the fact that bulky *t*-butyl groups have been replaced by methyl groups, these parameters agree reasonably well with the crystal structures of **1** and **1'**, respectively. As shown by the dihedral angle P–C7–C8–C9, the complexed phenyl ring and the adjacent C–C=P moiety form an angle that is appreciably larger in the determined crystal structure than in the optimized structure. Nevertheless, both the crystal structure and the DFT calculations indicate that complexation to $\text{Cr}(\text{CO})_3$ causes a drastic change of this dihedral angle.

A second set of calculations was performed with the reduced species. The optimized geometrical parameters calculated for (**1a**) $^-$ and (**1'a**) $^-$ are also included in Table 3. Reduction of **1a** and **1'a** causes an elongation of the P=C7 bond and a shortening (δ) of the C7–C8 bond which is more pronounced for the complex ($\delta = 0.055 \text{ \AA}$) than for the isolated phosphalkene ($\delta = 0.037 \text{ \AA}$). The most important structural changes due to the electron addition affect the $\text{Cr}(\text{CO})_3$ phenyl moiety of **1a**: this phenyl ring adopts an envelope conformation (C10–C12–C13–C8 = 9.9°) which removes the coplanarity of the C12, C13, C8, C7 atoms and contributes to an elongation of the Cr \cdots C8 distance (from 2.301 to 2.638 \AA), moreover the chromium atom moves away from C9 and C13 (Cr \cdots C9 increases from 2.252 to 2.382 \AA , Cr \cdots C13 increases from 2.255 to 2.380 \AA) while the Cr–C10, Cr–C11, Cr–C12 distances remain close to 2.25 \AA . These geometrical modifications clearly indicate that the anion formation causes a decrease

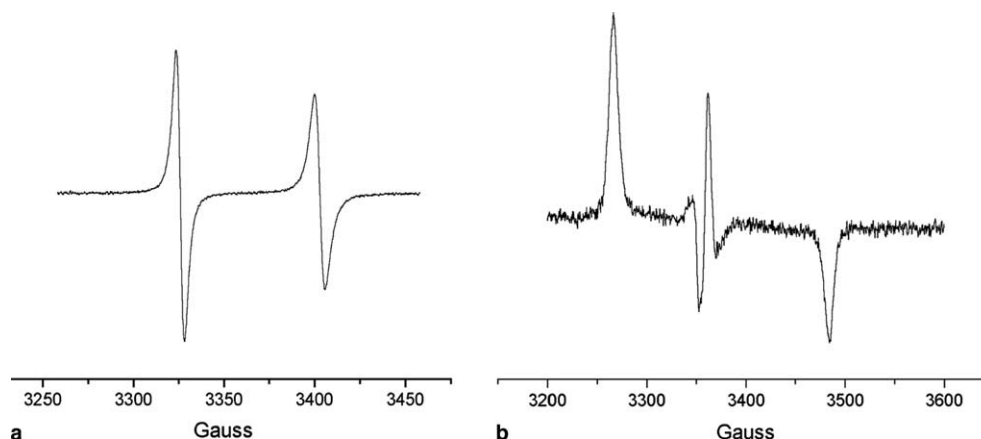


Fig. 3. Liquid solution (a) and frozen solution (b) EPR spectra obtained with a reduced solution of **1** in THF.

Table 2
Experimental EPR parameters^a and spin densities obtained for the reduction product of **1**

	<i>g</i> Values	³¹ P hyperfine coupling (MHz)			Phosphorus spin densities	
		T (³¹ P)	<i>A</i> _{iso}	τ (³¹ P)	<i>ρ</i> _s (P)	<i>ρ</i> _p (P)
Liquid solution	<i>g</i> = 2.0049		218 (152)			
Frozen solution	<i>g</i> = 1.9986 (2.003)	<i>T</i> = 603 (455)	221	<i>τ</i> = 382 (303)	0.016	0.52
	<i>g</i> _⊥ = 2.0075 (2.006)	<i>T</i> _⊥ = 29.5 (0.5)		<i>τ</i> _⊥ = -191.5 (-151.5)		
	<i>g</i> _{average} = 2.0045					

^a In parentheses experimental values for the non-complexed radical anion (**1'**)⁻ (see [1]).

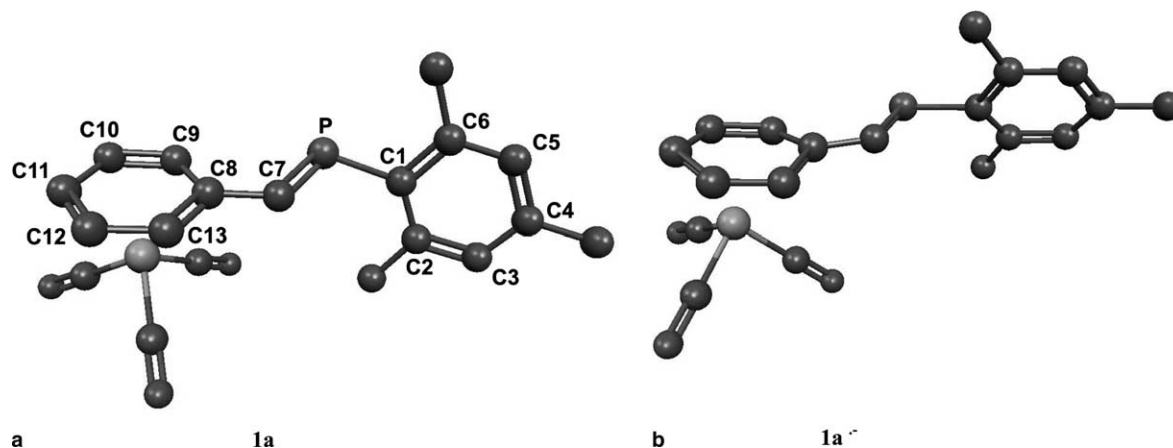


Fig. 4. Optimized structures for **1a** and **1a**⁻.

Table 3
Optimized parameters for the neutral and anionic complexes **1a** and (**1a**)⁻ and for the neutral and anionic non-complexed phosphalkenes **1'a** and (**1'a**)⁻

	Bond lengths (Å)			Bond angle (°)		Torsion angle (°)
	P=C7	C7-C8	P-C1	C7-P-C1	P-C7-C8-C9	C7-P-C1-C2
1a (Crystal 1) ^a	1.694 (1.666)	1.460 (1.477)	1.848 (1.852)	102.2 (100.5)	11.2 (25.4)	70.4 (89.9)
1'a (Crystal 1') ^b	1.695 (1.674)	1.462 (1.456)	1.856 (1.848)	101.6 (100.9)	-0.1 (-16)	92.2 (83.9)
(1a) ⁻	1.763	1.404	1.862	100.7	2.7	117.6
(1'a) ⁻	1.765	1.425	1.853	102.3	6.5	-131.4

^a This work.

^b From [21].

in the coordination number of chromium. As shown in Fig. 5 the relative orientation of the Cr(CO)₃ tripod and C_{ipso}-C(phosphaalkene)-bond changes with the reduction state: the system adopts a syn eclipsed conformation in the reduced species but is close to the anti-eclipsed conformation in the neutral species.

The *g* values and the hyperfine coupling constants have been calculated for the optimized structures of the complexed species (**1a**)⁻. For comparison, the coupling constants of the non-complexed phosphalkene radical anion **1a'**⁻ are also included in Table 4.

4. Discussion

As shown by cyclic voltammetry, Cr(CO)₃ complexation of the phenyl ring bound to a phosphalkene carbon facilitates the reduction of such a system. While the reduction of **1'** occurs at -1980 mV/SCE, the reduction wave of **1** occurs at -1550 mV/SCE.

The EPR parameters determined after electrochemical or chemical reduction of the Cr(CO)₃ complexed phosphalkene **1** are appreciably different from those previously reported for the non-complexed species **1a**. As expected,



Fig. 5. Orientation of the Cr(CO)₃ tripod with respect to the phenyl ring bound to the phosphalkene carbon.

Table 4
EPR parameters calculated by DFT for **(1a)^{•-}**

Basis set used for		³¹ P) <i>A</i> _{iso} (MHz)	Anisotropic couplings (MHz)			ρ_p	Diagonalized <i>g</i> -tensor
Optimization	Magnetic properties						
Set 1	6-31+G*	102.3	-170.2	-158.3	328.5	49.2	1.9907, 2.0069, 2.0081 ^a
	IGLO3	112.8	-182.7	-169.3	352.0	45.0	
	TZVP	130.8	-186.5	-174.8	361.3	48.0	
	TZVP ^b (for (1'a)^{•-})	92.1	-119.5	-111.1	230.6		
Set 2	Set 2	141.5	-169.5	-157.6	327.0	48.6	
Set 3	Set 3	142.1	-189.0	-176.3	365.3	49.9	
Set 4	Set 4	142.1	-189.0	-176.3	365.3	49.9	

^a Calculation with the 6-311++G** basis set: 1.9905, 2.0070, 2.0081.

^b Calculations (optimization and hyperfine couplings) for the non-complexed model **(1'a)^{•-}**.

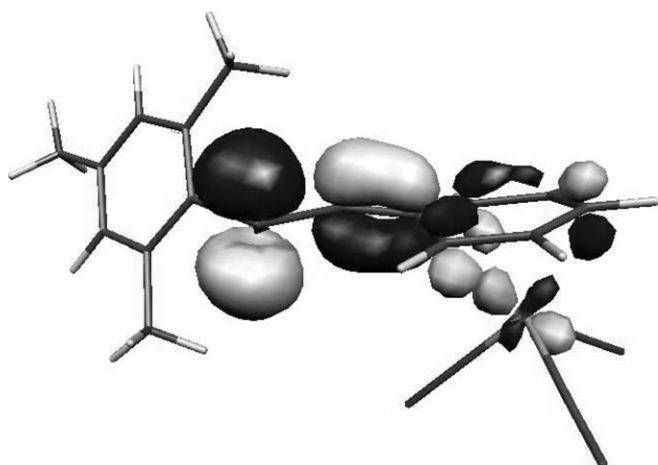
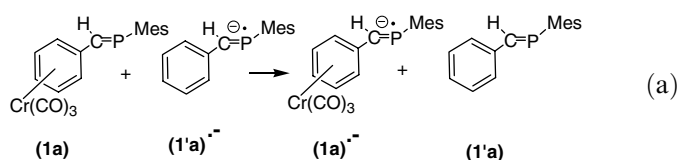


Fig. 6. Representation of the SOMO for **1a^{•-}**.

the presence of Cr(CO)₃ causes an increase of the *g* anisotropy ($\Delta g = g_{\parallel} - g_{\perp}$ increases from 0.0038 to 0.0089). The main difference between the two species lies in the enhancement of the phosphorus *p* _{π} spin density which leads to a marked enhancement in both the ³¹P isotropic coupling (*A*_{iso} increases from 152 to 217 MHz) and anisotropic constants (τ_{\parallel} increases from 303 to 386 MHz). The DFT calculations on the model compounds confirm the presence of the radical anion: the *g* tensor calculated for **1a^{•-}** very well agrees with the experimental values, while the calculated ³¹P dipolar coupling tensor is very close to the tensor reported in Table 2 for **1^{•-}**. The accord between experimental and calculated (³¹P)*A*_{iso} values is rather modest; but it is well known that the standard DFT methods perform rather poorly in predicting the Fermi contact interaction with ³¹P [32,33]. The DFT results confirm the effect of the presence of Cr(CO)₃ on the spin distribution, in particular, the stronger localisation of the unpaired electron on the phosphorus atom ($\rho_{\text{total,phosphorus}}$ increases from 0.37 to 0.64). The rather small spin density on the phosphalkene carbon explains why no spectral modification was observed with the corresponding ¹³C enriched compound. These properties, together with the NBO charge analysis (charge on the Cr(CO)₃-phenyl moiety = -0.577, on the phosphalkene carbon C7 = -0.45 [31]) suggest that a mesomeric form

which mainly contributes to the structure of **(1a)^{•-}** is a phosphinyl radical in which the phosphorus atom is bound to both a chromium-complexed benzylic anion and a Mes group. The SOMO calculated for **(1a)^{•-}** is represented in Fig. 6.

The homodestic equation (a) [34] was used to assess the effect of chromium tricarbonyl complexation on the stabilization of phosphalkene radical anion:



The molecular orbital stabilization energy, calculated by using the energy values calculated for the optimized structures of the reactants and products, is equal to 19 kcal mol⁻¹, therefore indicating that the complexation with chromium is a key stabilizing factor for the reduced phosphalkene. This value is, however, less than the stabilization (33 kcal mol⁻¹) previously reported for the benzylic anion. This stabilization is achieved through geometrical modifications that accompany the reduction of the complex **1a**: the chromium atom moves away from the exocyclic C8–C7 bond which gets some double bond character (the corresponding Wiberg bond order increases from 1.3 to 1.5 [31]); after rotation, the chromium tricarbonyl tripod adopts a syn eclipsed conformation with respect to the phosphalkene group. These geometric distortions allow a part of the negative charge to be localized on the Cr(CO)₃ moiety (charge on Cr(CO)₃ from NBO analysis: -0.4) [31].

5. Concluding remarks

Cr(CO)₃ complexation of the phenyl ring bound to a phosphalkenic carbon facilitates appreciably the reduction of the corresponding phosphalkene. In the resulting radical anion the presence of Cr(CO)₃ increases the spin density on the phosphorus atom as expected for a phosphinyl radical whose phosphorus is bound to a Cr(CO)₃ benzylic anion. Geometrical modifications related to the

formation of this anion lead to a stabilization of the paramagnetic species.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2005.08.045](https://doi.org/10.1016/j.jorganchem.2005.08.045).

References

- [1] M. Geoffroy, A. Jouaiti, G. Terron, M. Cattani-Lorente, Y. Ellinger, *J. Phys. Chem.* 96 (1992) 8241.
- [2] A. Al Badri, M. Chentit, M. Geoffroy, A. Jouaiti, *J. Chem. Soc., Faraday Trans.* 93 (1997) 3631.
- [3] A. Jouaiti, A. Al Badri, M. Geoffroy, G. Bernardinelli, *J. Organomet. Chem.* 529 (1997) 143.
- [4] F. Murakami, S. Sasaki, M. Yoshifuji, *J. Am. Chem. Soc.* 127 (2005) 8296.
- [5] C. Dutan, S. Shah, R.C. Smith, S. Choua, T. Berclaz, M. Geoffroy, *J.D. Protasiewicz, Inorg. Chem.* 42 (2003) 6241.
- [6] A. Jouaiti, M. Geoffroy, G. Terron, G. Bernardinelli, *J. Am. Chem. Soc.* 117 (1995) 2251.
- [7] A. Pfletschinger, T.K. Dargel, J.W. Bats, H-G. Schmalz, W. Koch, *Chem. Eur. J.* 2 (1999) 537.
- [8] C.A. Merlic, J.C. Walsh, D.J. Tantillo, K.N. Houk, *J. Am. Chem. Soc.* 121 (1999) 3596.
- [9] C. Merlic, B.N. Hietbrink, K.N. Houk, *J. Org. Chem.* 66 (2001) 6738.
- [10] A.F. Burchat, J.M. Chong, N. Nielsen, *J. Organomet. Chem.* 542 (1997) 281.
- [11] M. Yoshifuji, K. Toyota, K. Shibayama, N. Inamoto, *Chem. Lett.* 10 (1983) 1653.
- [12] A.H. Cowley, J.E. Kilduff, T.H. Newman, M. Pakulski, *J. Am. Chem. Soc.* 104 (1982) 5280.
- [13] E.P. Kuendig, A. Ripa, R. Liu, D. Amurrio, G. Bernardinelli, *Organometallics* 12 (1993) 3724.
- [14] R. Schreiner, A.B. Ellis, *J. Am. Chem. Soc.* 104 (1982) 3374.
- [15] W.C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* 43 (1978) 2923.
- [16] M. Yoshifuji, N. Inamoto, *Tetrahedron Lett.* 24 (1983) 4855.
- [17] M. Yoshifuji, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Chem. Soc., Chem. Commun.* (1985) 1109.
- [18] M. Yoshifuji, K. Toyota, N. Inamoto, *Tetrahedron Lett.* 26 (1985) 1727.
- [19] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 32 (1999) 115.
- [20] S.R. Hall, H.D. Flack, J.M. Stewart, *XTAL3.2 (User's Manual)*, Universities of Western Australia and Maryland, 1992.
- [21] R. Appel, J. Menzel, F. Knoch, P. Volz, *Z. Anorg. Allg. Chem.* 534 (1986) 100.
- [22] M. Yoshifuji, K. Toyota, I. Matsuda, T. Niitsu, N. Inamoto, *Tetrahedron* 44 (1988) 1363.
- [23] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03, Revision B.03*, Gaussian, Inc., Pittsburgh, PA, 2003.
- [24] A.D. Becke, *Phys. Rev. A.* 38 (1988) 3098.
- [25] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 54 (1988) 785.
- [26] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 270.
- [27] W. Kutzelnigg, C. van Willen, U. Fleischer, R. Franke, T. van Mourik, *NATO ASI Series*, 1993.
- [28] N. Godbut, D.R. Salahub, J. Andzelm, E. Wimmer, *Can. J. Chem.* 70 (1992) 560.
- [29] P. Flukiger, *Development of Molecular Graphics Package MOLEKEL*, Ph.D. Thesis, University of Geneva, Switzerland, 1992.
- [30] J.R. Morton, K.F. Preston, *J. Magn. Reson.* 30 (1978) 577.
- [31] See [Supplementary material](#).
- [32] S. Wesolowski, E. Johnson, M. Leininger, T. Crawford, H. Schaefer, *J. Chem. Phys.* 109 (1998) 2694.
- [33] N. Brinkmann, I. Carmichel, *J. Phys. Chem. A* 108 (2004) 9390.
- [34] P. George, M. Trachtman, C.W. Bock, A.M. Brett, *Theor. Chim. Acta* 38 (1975) 121.