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Structural assignment of the stable carbonylhydridotris-(triphenylphosphine)iridium(II) cation and spectroscopic and voltammetric identification of the transient Ir(III) dication and its decomposition pathway

Alan M. Bond *, David G. Humphrey, Dmitri Menglet, Georgii G. Lazarev, Ron S. Dickson, Truc Vu

> Department of Chemistry, Monash University, Clayton, Vic. 3168, Australia Received 9 September 1999; accepted 12 November 1999

Abstract

Detailed studies on the electrochemical oxidation of the 18-electron $IrH(CO)(PPh_3)_3$ complex have been undertaken in dichloromethane. Under voltammetric conditions, the process $IrH(CO)(PPh_3)_3 \rightleftharpoons [IrH(CO)(PPh_3)_3]^+ + e^-$, which leads to the formation of the 17-electron $[IrH(CO)(PPh_3)_3]^+$ cation, is chemically and electrochemically reversible. In contrast, the 16-electron dication $[IrH(CO)(PPh_3)_3]^{2+}$, formed by a further one-electron oxidation process, is very reactive and undergoes a rapid internal redox reaction, $[IrH(CO)(PPh_3)_3]^{2+} \rightleftharpoons [Ir(CO)(PPh_3)_3]^+ + H^+$, to form the stable 16-electron $[Ir(CO)(PPh_3)_3]^+$ species. In situ infrared (IR) spectroelectrochemical studies at low temperature, enable the v(CO) and v(IrH) IR bands to be obtained for $[IrH(CO)(PPh_3)_3]^+$ as well as for transiently formed $[IrH(CO)(PPh_3)_3]^{2+}$. EPR spectra obtained from frozen solutions of electrochemically generated $[IrH(CO)(PPh_3)_3]^+$ have been simulated. In agreement with results of density functional calculations on related $IrX(CO)(PPh_3)(X = H, Cl)$ complexes, the EPR data are consistent with $[IrH(CO)(PPh_3)_3]^+$ having a square pyramidal structure. Data are compared with those available for oxidation of the analogous RhH(CO)(PPh_3)_3 complex. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iridium(II) cation; Transient Ir(III) dication; Electrochemical oxidation; Voltammetric oxidation; 18-electron complex

1. Introduction

The 18-electron $M^{I}H(CO)(PPh_{3})_{3}$ complexes, where M = Rh or Ir, are important precursors to homogeneous catalysts [1,2]. Catalytic reactions involving these species are believed to occur via coordinatively unsaturated 16- or 14-electron species, which have been identified as reaction intermediates. However, we have characterised a moderately stable 17-electron monomeric $[RhH(CO)(PPh_{3})_{3}]^{+}$ species, which can be obtained by chemical or electrochemical oxidation of the 18-electron precursor [3]. An analysis of the EPR spectrum of this 17-electron species implied that

[RhH(CO)(PPh₃)₃]⁺ is an example of an uncommon paramagnetic monomeric rhodium(II) complex in which a structural change from trigonal bipyramidal to square pyramidal occurs upon oxidation of the rhodium(I) to the rhodium(II) complex. In this paper, we have extended our studies to the iridium analogue, where the 17-electron complex is stable and even the much more reactive 16-electron [IrH(CO)(PPh₃)]²⁺ dication is voltammetrically and spectroscopically detectable. EPR and IR spectra of the 17-electron $[IrH(CO)(PPh_3)]^+$ cation and IR spectra of [IrH(CO)(PPh₃)]²⁺ are reported. Results of density functional calculations on closely related Ir and Rh 17-electron species are consistent with the interpretation made on the basis of EPR spectra that a square pyramidal geometry is favoured for the one-electron oxidised form of the carbonyl hydrides. Finally, voltammetric

^{*} Corresponding author. Tel.: + 61-3-9905 4593; fax: + 61-3-9905 4597.

E-mail address: alan.bond@sci.monash.edu.au (A.M. Bond)

and spectroscopic studies have been undertaken to confirm that the transient 16-electron Ir(III) dication is rapidly converted to the Ir(I) complex $[Ir(CO)(PPh_3)_3]^+$, via an internal redox reaction. The results extend voltammetric and other data available on IrH(CO)-(PPh_3)_3 in acetonitrile-toluene and dichloroethane solutions [4,5].

2. Experimental

2.1. Materials

 $IrH(CO)(PPh_3)_3$ was prepared as described in the literature [6]. Dichloromethane was dried over CaH_2 and freshly distilled under a nitrogen atmosphere prior to use.

2.2. Electrochemical methods

Conventional voltametric measurements were carried out in dichloromethane solution (0.2 M ⁿBu₄NPF₆, ⁿBu₄NBF₄ or ⁿBu₄NClO₄) using a Cypress System model CS-1090 computer-controlled electroanalytical system or a BAS-100 electrochemical analyser. The working electrode was a platinum (d, 1.0 mm) or glassy carbon (GC) (d, 3.0 mm or 1.0 mm), the auxiliary electrode was a platinum wire and the reference electrode was Ag/AgCl (0.1 M ⁿBu₄NBF₄, dichloromethane-saturated LiCl) separated from the test solution by a salt bridge. The reversible voltammetry of an approximately 1.0 mM ferrocence (Fc) solution in the same solvent was used as a reference redox couple, and all potentials are quoted relative to Fc/Fc⁺. The electrolyte solutions were purged with nitrogen gas, and the cell was constantly maintained under an inert atmosphere. Rotating disc electrode voltammetry employed a variable speed rotator (Metrohm 628-10). Bulk electrolysis was carried out using a Bioanalytical System 100 electrochemical analyser. The bulk electrolysis cell contained two platinum baskets, which served as the working electrode and counter electrode and separated by a glass cylinder with porous glass frits in the base [7]. The reference electrode (Ag/Ag^+) was positioned as close as possible to the working electrode in order to maximise the uniformity of the potential over its surface. Digital simulation of cyclic voltammograms was performed with the simulation package DIGISIM V 2.1 (BAS, West Lafayette, IN) [8], run on a 150 MHz Pentium PC.

2.3. Spectroscopic methods

Infrared spectroelectrochemical experiments were carried out using a modified IR reflection-absorption spectroscopy (IRRAS) cell [9,10], mounted on a specular reflectance accessory located in the sample compartment of a Bruker IFS 55 FTIR spectrometer. The electrode arrangement consisted of a platinum wire working electrode, platinum gauze auxiliary electrode, and a silver wire pseudo reference electrode. Electrolyses were carried out by stepping the potential of the working electrode from a rest potential to a potential sufficient to cause electrolysis, typically 200 mV past the peak potential, and single-scan IR spectra (resolution 1.0 cm⁻¹) were collected as a function of time. Electrolyses in IRRAS experiments were performed with a Princeton Applied Research (PAR) (Princeton, NJ) model 174A Polarographic Analyser. The dichloromethane (0.2 M ⁿBu₄NPF₆) electrolyte solutions were prepared as for the voltammetric experiments, and solutions were deoxygenated before syringing into the IRRAS cell. The cell itself was thoroughly flushed with nitrogen prior to addition of the samples and maintained under a nitrogen atmosphere throughout the experiments.

3. Results and discussion

3.1. Electrochemistry of IrH(CO)(PPh₃)₃

Cyclic voltammograms of the IrH(CO)(PPh₃)₃ in dichloromethane solution (0.2 M ⁿBu₄NPF₆) at a GC disc macro-electrode (d, 1.0 mm) over the scan rates of 1.0-0.05 V s⁻¹ at 20 \pm 2°C, reveal the presence of an initial reversible one-electron oxidation process, which has a reversible potential ($E_{1/2}^{r}$ -value) of -0.47 V versus Fc/Fc⁺. The analogous process obtained from oxidation of the Rh complex has a reversible potential of -0.48 V versus Fc/Fc⁺ [3]. Data obtained for this process as a function of scan rate are summarised in Table 1. Comparison of experimental and simulated responses (Fig. 1), confirms that the first process is reversible in both the chemical and electrochemical senses. Importantly, the voltammetry is unaffected by the presence of up to a 20-fold concentration excess of triphenylphosphine. In regard to thermodynamics, this result implies that the equilibrium position for the reaction shown in Eq. (1), and the analogous reaction for the oxidised form of the compound, must lie a long way to the left in dichloromethane. The voltammetry also remains unchanged in the presence of up to 30-fold molar excess of AsPh₃, which indicates that no ligand exchange is taking place.

 $IrH(CO)(PPh_3)_3 \rightleftharpoons IrH(CO)(PPh_3)_2 + PPh_3$ (1)

The initial voltammetric oxidation process therefore can be assigned to the reaction given in Eq. (2).

$$\operatorname{Ir}^{I}H(CO)(PPh_{3})_{3} \rightleftharpoons [\operatorname{Ir}^{II}H(CO)(PPh_{3})_{3}]^{+} + e^{-}$$
 (2)

Table 1

Cyclic voltammetric data obtained for the oxidation of $IrH(CO)(PPh_3)_3$ (4 mM) in dichloromethane (0.2 M nBu_4NPF_6) at a GC macro-disc electrode (d, 3.0 mm)

Scan rate (mV s ⁻¹)	$E_{\rm pa}$ (V)	$E_{\rm pc}$ (V)	$E_{1/2}^{\rm r}$ ^a (V)	i _{pa} (mA)	$i_{\rm pa}/i_{\rm pc} \ ^{\rm b}$
First oxidation process					
50	-0.43	-0.52	-0.47	42	0.53
100	-0.42	-0.52	-0.47	59	0.56
200	-0.41	-0.53	-0.47	82	0.75
500	-0.39	-0.56	-0.47	125	0.93
1000	-0.36	-0.58	-0.47	170	0.96
5000	-0.27	-0.67	-0.47	330	0.98
Second oxidation process					
50	0.02	-0.08	-0.03	36	0.32
100	0.03	-0.08	-0.03	55	0.45
200	0.05	-0.08	-0.01	70	0.70
500	0.08	-0.10	-0.01	100	0.94
1000	0.12	-0.11	-0.01	143	0.95
5000	0.23	-0.17	-0.01	270	0.96

^a The assumption that $E_{1/2}^r = (E_{pa} + E_{pc})/2$ is only strictly correct for the second process for data obtained at fast scan rates when this process is chemically as well as electrochemically reversible.

^b This ratio is close to 1.0 for the first oxidation process if the potential is switched after the first oxidation process. Data reported refer to results obtained when the potential is switched after the second process.

If the potential of the glassy carbon electrode is scanned to the negative potential region on the reverse scan, switching the potential just after the initial oneelectron oxidation process, no additional electrochemical processes are observed. However, if the potential is scanned beyond the first process, a second one-electron oxidation process is observed at about -0.01 V versus Fc/Fc⁺ (Fig. 2). Now, on the reverse scan, a reversible two-electron process is observed at -1.57 V versus Fc/Fc⁺. This process may be assigned to formation and then two electron reduction of the [Ir^I(CO)(PPh₃)₃]⁺ species [11]. The electrochemical behaviour for the second oxidation step is therefore readily shown to be of the EC type as described in Eq. (3).

$$[Ir^{II}H(CO)(PPh_3)_3]^* \rightleftharpoons [Ir^{III}H(CO)(PPh_3)_3]^{2^*} + e^{-k_1} k_1$$

$$k_1 k_1$$
(3)

 $[Ir^{I}(CO)(PPh_{3})_{3}]^{+} + H^{+}$

The voltammetric data obtained in dichloromethane are summarised in Table 1 and are generally consistent with earlier studies which were undertaken in acetonitrile/toluene and dichloroethane media [4,5]. However, unlike the case in dichloroethane, in dichloromethane this second process is not fully reversible in the chemical sense at slow scan rates (cyclic voltammetry) or slow rotation rates (rotating disc electrode voltammetry) at 20°C. Furthermore, the nature of the electrolyte anion (PF_6^- , BF_4^- and ClO_4^-) is crucial to the degree of chemical reversibility as well as scan rate and temperature. Maximum chemical reversibility for the second process was detected at fast scan rates or at low temperatures with 0.2 M ⁿBu₄NPF₆ (Fig. 2) as the electrolyte, whilst with 0.2 M ⁿBu₄NClO₄ as the electrolyte, greater chemical reversibility is seen at slow scan rates than at fast scan rates. The degree of reversibility of the second oxidation process with respect to electrolyte dependence is in the order: ⁿBu₄NPF₆ > ⁿBu₄NBF₄ > ⁿBu₄NClO₄. Finally, it was noted that voltammetry at the platinum electrode is more complicated than at the glassy carbon because of the presence of H⁺ and the low over-potential of the 2H⁺ \rightarrow H₂ + 2e⁻ process at platinum.

Clearly, the formally 16-electron $[Ir^{III}H(CO)-(PPh_3)_3]^{2+}$ dicationic species undergoes overall reductive elimination of a proton on long time scale voltammetric reduction experiments according to the reaction shown in Eq. (4). This fact is evidenced by the generation of a reduction process (Eq. (5)) at very negative potentials after scanning of the potential is



Fig. 1. Comparison of (a) experimental and (b) simulated cyclic voltammograms at 20°C for the initial one-electron oxidation process of IrH(CO)(PPh₃)₃ (4 mM) in dichloromethane (0.2 M ⁿBu₄NPF₆) at a GC macro-disc electrode (d, 1.0 mm) using a scan rate of 100 mV s⁻¹. Simulations were undertaken with a diffusion coefficient value of 5×10^{-6} cm² s⁻¹, a double-layer capacitance of 1×10^{-7} F cm⁻² and uncompensated resistance of 1200 Ω .



Fig. 2. Voltammograms over a wide potential range for oxidation of $IrH(CO)(PPh_3)_3$ (4 mM) in dichloromethane (0.2 M ⁿBu₄NPF₆) at a GC macro-electrode (d, 3.0 mm). (a) Cyclic voltammogram at a scan rate of 200 mV s⁻¹ and (b) rotated disc voltammogram at a scan rate of 10 mV s⁻¹ and rotation rate of 500 rpm.

Table 2 IR spectroscopic data ^a

Complex	$v(CO) (cm^{-1})$	$v(\text{IrH}) \text{ (cm}^{-1})$
$[IrH(CO) (PPh_3)_3] [IrH(CO)(PPh_3)_3]^+ [IrH(CO)(PPh_3)_3]^{2+} [Ir(CO)(PPh_3)_3]^+$	1924 ^b 1988 ^b 2068 ^c 2017 ^b	2071 ^b 2104 ^b 2176 ^c

^a Recorded in an IRRAS cell in dichloromethane (0.2 M $^{n}Bu_4NPF_6$).

^b Electrogenerated at 20°C.

^c Electrogenerated at -45°C.

reversed at more positive values than for the second process under conditions when the second process is chemically irreversible (Fig. 2).

$$[Ir^{III}H(CO)(PPh_3)_3]^2 \xrightarrow{\kappa_1} [Ir^I(CO)(PPh_3)_3]^+ + H^+$$
(4)

$$[\operatorname{IrH}(\operatorname{CO})(\operatorname{PPh}_3)_3]^2 + 2e^-$$

$$\rightleftharpoons [\operatorname{Ir}(\operatorname{CO})(\operatorname{PPh}_3)_3]^- + H^+ \underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\underset{k_{-2}}{\overset{k_2}{\underset{k_{-2}}{\underset{k_{-2}}{\overset{k_{-2}}{\underset{k_{-2}}{\overset{k_{-2}}{\underset{k_{-2}}}{\underset{k_{-2}}{\underset{k_{-$$

The iridium 16-electron dication is considerably more stable on the voltammetric time scale than its rhodium analogue [3], where no reduction component is associated with the second oxidation process, even at fast scan rates and low temperatures.

Bulk electrolysis of $IrH(CO)(PPh_3)_3$ in dichloromethane (0.2 M ⁿBu₄NBF₄ or 0.2 M ⁿBu₄NClO₄) at 20°C at potentials between the first and second oxidation processes (-0.22 V versus Fc/Fc⁺) requires 1 equiv. of electrons per mole of complex. However, this experiment results in about an equimolar mixture of $[IrH(CO)-(PPh_3)_3]^+$ and $[Ir(CO)(PPh_3)_3]^+$ as calculated on the basic of voltammetric peak heights obtained after electrolysis. Electro-regeneration of $IrH(CO)(PPh_3)_3$ is effected by holding the potential at -1.9 V versus Fc/Fc⁺, but only about 40% of the starting material is recovered. Bulk electrolysis on the plateau of the second oxidation process (0.5 V versus Fc/Fc⁺) requires 2 equiv. of electrons per mole of complex and $[Ir(CO)(PPh_3)_3]^+$ is the final product. These data also imply that $[IrH(CO)(PPh_3)_3]^+$ is not completely stable and that on long time scales, the reaction given in Eq. (6) occurs. The presence of other minor side reactions is also indicated [4,5].

 $[Ir^{II}H(CO)(PPh_3)_3]^+ \rightarrow [Ir^{I}(CO)(PPh_3)_3]^+ + 1/2H_2\uparrow \quad (6)$

3.2. IR spectroelectrochemistry

The IR spectrum of $[IrH(CO)(PPh_3)_3]$ contains two bands at 1924 and 2071 cm⁻¹, which can be assigned to v(CO) and v(IrH), respectively [4,12] (Table 2). Upon oxidation in an IRRAS cell at -0.22 V versus Fc/Fc⁺ at 20°C, the spectral changes shown in Fig. 3(a) occur. In this and other IR spectroelectrochemical experiments, the absorbance, relative to that of the parent complex, is plotted as a function of wavenumber (i.e. the difference spectrum). Those bands that appear to grow in Fig. 3(a) by giving negative absorbance differences at 1924 and



Fig. 3. Changes in the IR difference spectra accompanying the oxidation of 2 mM $IrH(CO)(PPh_3)_3$ in an IRRAS cell in dichloromethane (0.2 M nBu_4NPF_6). (a) First oxidation at 20°C and (b) second oxidation process at $-45^{\circ}C$.

2071 cm⁻¹ signify that depletion of $[IrH(CO)(PPh_3)_3]$ occurs within the thin-layer, whilst those that grow with a positive absorbance difference at 1988 and 2104 cm⁻¹ are attributed to the formation of the product, $[IrH(CO)(PPh_3)_3]^+$. The changes in the IR spectra occur with retention of isobestic points and re-reduction quantitatively regenerates the starting spectrum in its entirety, such that the one-electron $[IrH(CO)(PPh_3)_3]^{+/0}$ process is fully reversible under the experimental conditions and on the time scale of the IR spectroelectrochemical experiment. Reactions that occur on very long time scales (10–20 min) of bulk electrolysis experiments (Eq. (6)) do not influence either voltammetric or rapid thin-layer electrolysis experiments.

If, after electrogeneration of $[IrH(CO)(PPh_3)_3]^+$ at ambient temperature (20°C), the potential of the working electrode is stepped to +0.1 V versus Fc/Fc⁺ in order to cause the second oxidation step to occur, the bands at 1988 and 2104 cm⁻¹ collapse and they are replaced by a single band at 2017 cm⁻¹. In this case returning the potential of the working electrode to -0.22 V does not cause any reductive current to flow through the cell, nor do any further spectral changes occur. Thus, the one-electron oxidation of [IrH(CO)- $(PPh_3)_3$ ⁺ is chemically irreversible on the time scale of IR spectroelectrochemical experiments conducted at 20°C. The product formed from an overall two-electron oxidation is $[Ir(CO)(PPh_3)_3]^+$, as identified by the wavenumber of 2017 cm⁻¹ for the v(CO) band [13]. This result is consistent with the conclusion made on the basis of voltammetric data (Fig. 2).

If the oxidation of $[IrH(CO)(PPh_3)_3]^+$ is carried out at low temperature $(-45^{\circ}C)$, the spectral changes shown in Fig. 3(b) occur, and they are very different to those observed at 20°C. In this low-temperature study, the bands due to [IrH(CO)(PPh₃)₃]⁺ at 1988 and 2104 cm^{-1} collapse with the growth of new bands at 2068 and 2176 cm⁻¹. If the electrolysis is stopped after oxidation of approximately 20% of [IrH(CO)(PPh₃)₃]⁺, and the potential of the working electrode returned to -0.22 V, then [IrH(CO)(PPh₃)₃]⁺ is quantitatively regenerated. Conversely, if the oxidation is allowed to continue past this point, isobestic points are lost and the starting spectrum cannot be fully regenerated. The bands at 2068 and 2176 cm⁻¹ are attributed to the formation of the transient dication. [IrH(CO)- $(PPh_3)_3]^{2+}$, which is moderately stable at low temperature, but which is rapidly deprotonated at room temperature. This appears to be the first time the IR spectrum of $[IrH(CO)(PPh_3)_3]^{2+}$ has been observed.

3.3. EPR spectroscopy

An EPR spectrum of the one-electron oxidised $[Ir^{II}(H)(CO)(PPh_3)_3]^+$ cation has been reported in the

literature [12]. However, the details of the spectrum have not been assigned, via comparison with simulated spectra.

The $[Ir^{II}H(CO)(PPh_3)_3]^+$ cation was electrogenerated by bulk electrolysis at a platinum basket electrode in dichloromethane for the EPR measurements at a potential of -0.22 V versus Fc⁺/Fc, which was approximately 0.25 V more positive than the reversible potential of the first oxidation process but still well removed from the potential of the second oxidation process. The electrogeneration was carried out at both low (approximately -45° C) and ambient temperature in dichloromethane, but this had no effect on the EPR spectrum of the product. Fortunately, any diamagnetic $[Ir^{I}(CO)(PPh_3)_3]^+$ formed as in Eq. (6) does not cause a problem with respect to the measurement and interpretation of EPR spectra of the paramagnetic $[Ir^{II}H(CO)(PPh_3)_3]^+$.

A frozen dichloromethane (0.2 M ⁿBu₄NBF₄) EPR spectrum at 77 K obtained from the electrochemically generated [Ir^{II}H(CO)(PPh₃)₃]⁺ species is presented in Fig. 4(a) and is consistent with the literature [12]. The EPR signal consists of several lines, which is expected from the strong anisotropy of the g-value and the presence of hyperfine structure. The signal manifold exhibits some resemblance to that obtained with the rhodium analogue [3], even though it appears to be apparently less complex. Comparisons with simulated spectra suggest that the EPR response of $[Ir^{II}H(CO)(PPh_3)_3]^+$ is constructed from two similar sets of lines (A, B, C and D, E, F in Fig. 4), each set corresponding to a significant anisotropy of the gvalue. However, for the Ir complex, the lines B and D partly overlap, as do E and C. As in the case with the rhodium analogue, the splitting between the two sets of lines is attributed to strong hyperfine interaction of the unpaired electron in a low spin Ir(II) complex with either a P or H nucleus, possessing a nuclear spin of 1/2. Further hyperfine splitting can be discerned in the quartets C and F, which must arise from the interaction of the unpaired electron with the Ir metal atoms having nuclear spin of 3/2.

The anisotropy of the *g*-value for the $[Rh^{II}H(CO)(PPh_3)_3]^+$ complex [3], may be accounted for by assuming a pseudo square pyramidal structure with a phosphorus atom at the apex (C_s symmetry). With this geometry, the splitting between the two sets of lines (A, B, C and D, E, F) is caused by the hyperfine coupling with the apical phosphorus, which is then amplified by the mixing of the singly occupied rhodium orbital and the apical phosphorus s orbital.

Computer simulation of the EPR spectrum using the Bruker 'SIMFONIA' program was undertaken in order to confirm that a similar interpretation applies to the



Fig. 4. (a) (i) Experiment and (ii) simulated EPR spectra of (a) $[Ir^{II}H(CO)(PPh_3)_3]^+$ and (b) $[Ir^{II}Cl(CO)(PPh_3)_3]^+$.



Fig. 5. Predicted [17] changes in the geometric structure and frontier orbital domain accompanying the oxidation of the IrH(CO)(PPh₃)₃ to the [Ir^{II}H(CO)(PPh₃)₃]⁺ complex: widening of the angle α lifts the degeneration of the two highest occupied d orbitals. In the new geometry, the HOMO, by convention, is assigned as the d₂ orbital.



Fig. 6. Computed[17] pseudo square pyramidal structure for $[Ir^{II}H(CO)(PH_3)_3]^+$.

spectrum of $[Ir^{II}H(CO)(PPh_3)_3]^+$ and to quantify the values of the EPR parameters. Fig. 4(a(ii)) illustrates the result of the simulation with the following parameters: $g_1 = 2.219$, $g_2 = 2.147$, $g_3 = 1.975$; $A(P_{ap})_1 = 140.0$ G; $A(P_{ap})_2 = 147.0$ G; $A(P_{ap})_3 = 200.0$ G (P nucleus, spin 1/2); $A(Ir)_1 = 8.0$ G; $A(Ir)_2 = 7.0$ G; $A(Ir)_3 = 39.0$ G (Ir nucleus, spin 3/2); line-widths for one, two and three components are 15.0, 10.0 and 10.0 G, respectively. A Gaussian line-shape was used in the simulation and the comparison with experimental results is excellent.

A frozen solution EPR spectrum of the species prepared chemically by oxidation with the ferrocenium cation in dichloromethane, rather than by controlled potential electrolysis, represents the superimposition of the above spectrum and residual ferrocenium cation.

An EPR spectrum of the related $[Ir^{II}Cl(CO)(PPh_3)_3]^+$ cation has also been reported in the literature (Fig. 4(b)) [14]. The spectrum bears a strong resemblance to that of the hydride analogue. However, an important difference is that the lines C and F now appear to be more like triplets rather than quartets, which may be explained if hyperfine interaction with the two in-plane phosphorus atoms takes precedence over iridium coupling. The description of the original EPR signal for [Ir^{II}Cl(CO)(PPh₃)₃]⁺ solely in terms of two g-values of 2.128 and 2.00 therefore seems to represent an over simplification. Fig. 4(b(ii)) presents the result of a computer simulation with the following parameters: $g_1 =$ 2.3300, $g_2 = 2.2370$, $g_3 = 2.0640$; $A(P_{ap})_1 = 180.0$ G; $A(P_{ap})_2 = 182.0 \text{ G}; A(P_{ap})_3 = 235.0 \text{ G}; A(P_{eq})_1 = 18.0 \text{ G};$ $A(P_{eq})_2 = 8.0$ G; $A(P_{eq})_3 = 33.0$ G (two nuclei); linewidths for one, two and three components are 15.0, 10.0 and 10.0 G, respectively. Again, Gaussian line-shape was used in the simulation and the comparison with experimental results is excellent.

3.4. Density functional calculations

Results [17] of density functional calculations on the $[Ir^{II}X(CO)(PH_3)_3]^+$ (X = H or Cl) and the $[Rh^{II}H(CO)(PH_3)_3]^+$ cations also suggest that $[Ir^{II}X(CO)(PPh_3)_3]^+$ complexes are likely to have square pyramidal structures with a phosphorus atom in the apex and the other two P atoms trans to each other. In reaching this conclusion, it is assumed that the more calculation complex. from the perspective, $[Ir^{II}X(CO)(PPh_3)_3]^+$, would produce analogous results to those undertaken with [Ir^{II}X(CO)(PH₃)₃]⁺. Indeed, all d⁷ trigonal bipyramidal complexes would be Jahn-Teller unstable and may therefore be expected to rearrange by widening the P-Ir-P or P-Rh-P angle [15,16] (Fig. 5), which results in the calculated pseudo square pyramidal structure shown in Fig. 6 [17].

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