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Oxidation of the Carbonylbis(1,2-bis(diphenylphosphino)ethane)iridium(I) Cation. Preparation and Characterization of a Series of Iridium(III) Carbonyl Dications

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Oxidation of $Ir(CO)(dppe)_2^+$ with halogens affords *cis*-$IrX(CO)(dppe)_2^{2+}$ (X = Cl, Br) while oxidation with HBF_4 affords *cis*-$IrH(CO)(dppe)_2^{2+}$. The species *trans*-$IrX(CO)(dppe)_2^{2+}$ (X = Cl, Br) are prepared by the oxidation of $Ir(CO)(dppe)_2^+$ with nitrosonium ion in the presence of Cl^- or Br^-. The complex *trans*-$IrH(CO)(dppe)_2^{2+}$ is most conveniently prepared by protonation of $[Ir(dppe)_2]BF_4$ with $HBF_4 \cdot Et_2O$ to afford the intermediate $IrH(dppe)_2^{2+}$, followed by CO addition. In contrast, both *cis*- and *trans*-$IrCl(CO)(dppe)_2^{2+}$ species are formed by the electrochemical oxidation of $Ir(CO)(dppe)_2^+$ in chloride media. The trans isomer is reduced at a more negative potential and is thus thermodynamically the more stable. Reversible deprotonation of *cis*-$[IrH(CO)(dppe)_2][BF_4]_2$ by chloride implies that the acidity of this compound is of the order of that of HCl, unusually strong for a third-row transition-metal hydrido complex.

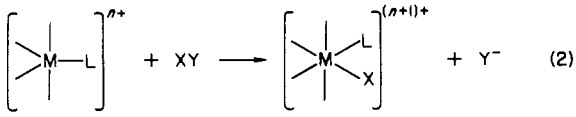
Introduction

The catalytic activity of d^8 metal complexes in important reactions such as hydrogenation and hydroformylation has led to much research on the basic processes that take place at a transition-metal center.[1,2] Oxidative-addition reactions figure prominently in homogeneously catalyzed transformations of organic substrates.[3] As a result, much information has been gathered on oxidative-addition reactions of four- and five-coordinate d^8 metal complexes.[2]

Previous studies on the oxidation of five-coordinate complexes have shown two general modes of reaction.[2a,b] The first mode involves initial loss of ligand to afford a coordinatively unsaturated four-coordinate complex that then reacts with the addendum (eq 1). This mode of reactivity is typical of ox-

$$ML_5 \rightleftharpoons ML_4 + L \xrightarrow{XY} ML_4XY \qquad (1)$$

idative-addition reactions that involve nonpolar addenda such as H_2 or olefins.[4] The second mode of oxidation of five-coordinate d^8 complexes, that shown in eq 2 and 3, is typical of



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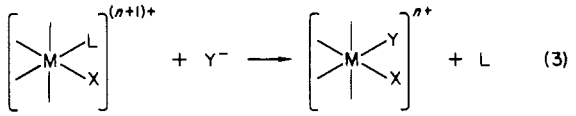
A



(3)

A B

oxidations by HX, halogens, or other electrophiles. Oxidation affords a cationic, octahedral d^6 complex (A), in which part of the addendum (Y) serves as counterion. Complexes of type A are not usually isolated owing to a subsequent reaction (eq 3) in which Y displaces a neutral ligand L (e.g., CO, PR_3) to give the observed product (B).[4a,5]

A carbonyl ligand is often labilized on oxidation of a transition-metal complex.[6] This increased lability is a result of decreased π donation of electron density from metal $d\pi$ orbitals to carbonyl π^* orbitals. Consequently, few carbonyl complexes of type A are stable in the presence of coordinating counterions,[7] making difficult their preparation according to eq 2. Successful preparations of complexes of type A have been realized either when Y is a noncoordinating anion, as in reactions with HBF_4 or HPF_6, or when the metal is ligated with tightly binding ligands, such as alkyl isocyanides.[5a,8] A second effect of decreased π bonding in the oxidized complexes is the predisposition of the carbonyl carbon atom to nucleophilic attack.[9] Thus, isolable carbonyl complexes of type A are of interest as they may be effective in carbon monoxide activation.

In this work we describe straightforward syntheses of a class of dicationic iridium(III) carbonyl complexes, *cis*- and *trans*-$IrX(CO)(dppe)_2^{2+}$ (X = Cl, Br, H).[10] H).[10] With the correct choice of reagents, cis and trans isomers are easily and selectively prepared by oxidation of $Ir(CO)(dppe)_2^+$. These complexes are stable toward CO loss and are readily isolated. The reactivity of these complexes toward nucleophiles is the subject of a forthcoming report.[11]

Experimental Section

All reactions were carried out under an atmosphere of prepurified nitrogen with the use of standard Schlenk line techniques. Solvents

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(10) Abbreviations: dppe = $Ph_2PCH_2CH_2PPh_2$; dppp = $Ph_2PCH_2CH_2CH_2PPh_2$; Cp = η^5-C_5H_5; Et = C_2H_5; Ph = C_6H_5; s = singlet; d = doublet; q = quintet; m = multiplet; br = broad.

(11) Lilga, M. A.; Ibers, J. A., submitted for publication.

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were purified by standard methods. CO, HCl, Cl_2, and NOCl were obtained from Matheson Gas, Inc., and used as received.

Elemental analyses were conducted by Galbraith Laboratories, Inc., Knoxville, TN, and by Schwarzkopf Microanalytical Laboratories, Woodside, NY. Infrared spectra, obtained as Nujol mulls, were recorded on a Perkin-Elmer 283 spectrometer. Spectra below 400 cm^{-1} were recorded with the use of CsI or polyethylene plates. ^1H and $^{31}P\{^1H\}$ spectra were obtained on a JEOL FX90Q spectrometer. Positive $^{31}P\{^1H\}$ chemical shifts are downfield from 85% H_3PO_4.

Syntheses. $[Ir(CO)(dppe)_2]Cl$ (Ia) and $[Ir(dppe)_2]Cl$ were prepared by published procedures.[12] $[Ir(CO)(dppe)_2]BF_4$ (Ib) and $[Ir(dppe)_2]BF_4$ were prepared by metathesis with NH_4BF_4, as described below. $[Ir(dppe)_2]Cl$ was also prepared as follows. To $Ir_2Cl_2(C_8H_{14})_4$, prepared from $IrCl_3 \cdot xH_2O$ (5.01 g, 14.2 mmol), was added 180 mL of degassed benzene. A solution of dppe (11.0 g, 27.6 mmol) dissolved in 100 mL of degassed benzene was added and the reaction mixture stirred for 30 min. The orange precipitate was filtered, washed with benzene and ether, and dried in vacuo overnight; yield (based on $IrCl_3 \cdot xH_2O$) 55%. The product was identified on the basis of spectral comparison with an independently prepared sample.

Tetrafluoroborate salts of iridium cations were prepared by addition of NH_4BF_4 in CH_3CN to a solution of the chloride salt of the iridium complex dissolved in 1:1 CH_2Cl_2/CH_3CN. In a typical preparation the solution was stirred for 0.5 h and filtered, and the solvent was removed from the filtrate. Recrystallization from CH_2Cl_2 gave the desired product.

***cis*-[IrCl(CO)(dppe)$_2$]X$_2$ (II).** $[Ir(CO)(dppe)_2]Cl$ was dissolved in 5 mL of CH_2Cl_2 and the solution saturated with CO. Cl_2 was then bubbled through the solution. Addition of THF gave a white precipitate of *cis*-$[IrCl(CO)(dppe)_2]Cl_2$ (IIa), which was filtered, washed with tetrahydrofuran (THF), and dried in vacuo. Metathesis with NH_4BF_4 and recrystallization from CH_2Cl_2/THF gave *cis*-$[IrCl(CO)(dppe)_2][BF_4]_2$ (IIb) in 80% yield. ^1H NMR (CD_2Cl_2): δ 3.9 (methylene, br), 6.4 (phenyl, dd, J = 11.8, 8.7 Hz), 6.6–8.5 (phenyl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_A 15.4, δ_B 10.9, δ_C 3.7, δ_D −3.3 (J_{AB} = 7.3 Hz, J_{AC} = 266.8 Hz, J_{AD} = 3.5 Hz, J_{BC} = 6.1 Hz, J_{BD} = 14.7 Hz, J_{CD} = 18.3 Hz). Anal. Calcd for $C_{53}H_{48}B_2ClF_8IrOP_4$: C, 51.92; H, 3.95; P, 10.10. Found: C, 51.91; H, 3.96; P, 9.72.

***cis*-[IrBr(CO)(dppe)$_2$]X$_2$ (III).** III was prepared in a manner analogous to the preparation of II except for the use as oxidant of Br_2 in place of Cl_2 to afford *cis*-$[IrBr(CO)(dppe)_2]Br_2$ (IIIa). Metathesis and recrystallization gave *cis*-$[IrBr(CO)(dppe)_2][BF_4]_2$ (IIIb). ^1H NMR (CD_2Cl_2): δ 3.7 (methylene, br), 6.4 (phenyl, dd, J = 12.3, 7.7 Hz), 6.6–8.3 (phenyl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_A 14.1, δ_B 11.2, δ_C 3.1, δ_D −7.1 (J_{AB} = 6.7 Hz, J_{AC} = 3.4 Hz, J_{AD} = 14.3 Hz, J_{BC} = 269.8 Hz, J_{BD} = 6.1 Hz, J_{CD} = 17.1 Hz). Anal. Calcd for $C_{53}H_{48}B_2BrF_8IrOP_4$: C, 50.10; H, 3.81. Found: C, 50.63; H, 3.97.

***cis*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (IV).** $[Ir(dppe)_2]BF_4$ was dissolved in 10 mL of CH_2Cl_2 and the solution saturated with CO. Excess $HBF_4 \cdot Et_2O$ was added dropwise. Addition of ether precipitated the desired product, which was recrystallized from CH_2Cl_2/Et_2O. ^1H NMR ($CDCl_3$): δ −9.7 (hydride, dm, $J_{H-P(trans)}$ = 104 Hz), 3.0 (methylene, br), 6.13, 6.49 (phenyl, dd, J = 11.6, 7.7 Hz), 7.6–6.8 (phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_A 31.1, δ_B 20.6, δ_C 15.3, δ_D 2.4 (J_{AB} = 7.3 Hz, J_{AC} = 228.3 Hz, J_{AD} = 12.2 Hz, J_{BC} = 19.5 Hz, J_{BD} = 17.1 Hz, J_{CD} = 1.5 Hz). Anal. Calcd for $C_{54}H_{50}B_2Cl_3F_8IrOP_4$ (sample contains ca. 1 equiv of $CHCl_3$): C, 49.48; H, 3.84. Found: C, 47.70; H, 3.79.

***trans*-[IrCl(CO)(dppe)$_2$]X$_2$ (V). Method A:** $[Ir(dppe)_2]Cl$ (0.45 g, 0.44 mmol) was dissolved in 5 mL of CH_2Cl_2 and the solution saturated with CO. NOCl gas was then bubbled through the solution. Addition of THF gave a white precipitate of *trans*-$[IrCl(CO)(dppe)_2]Cl_2$ (Va), which was filtered, washed with THF, and dried in vacuo. Metathesis with NH_4BF_4 and recrystallization from CH_2Cl_2/Et_2O gave *trans*-$[IrCl(CO)(dppe)_2][BF_4]_2$ (Vb) in 90% isolated yield. ^1H NMR (CH_2Cl_2): δ 3.0 (methylene, br), 6.7–7.7 (phenyl). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 11.2 (s). Anal. Calcd for $C_{53}H_{48}B_2ClF_8IrOP_4$: C, 51.92; H, 3.95; Found: C, 52.27; H, 3.90.

Method B: A CO-saturated solution of $[Ir(dppe)_2]Cl$ (0.20 g, 0.20 mmol) in 10 mL of CH_2Cl_2 was added to $[FeCp_2]BF_4$ (0.11 g, 0.43 mmol) in 5 mL of CH_2Cl_2. The solution was purged with CO and stirred overnight. The off-white precipitate that formed on addition of THF was filtered and the material was recrystallized several times from CH_2Cl_2/THF to give *trans*-$[IrCl(CO)(dppe)_2][BF_4]_2$ (Vb).

***trans*-[IrBr(CO)(dppe)$_2$][BF$_4$]$_2$ (VI).** A solution of $[Ir(CO)(dppe)_2]Br$ (0.083 g, 0.076 mmol), dissolved in 3 mL of CH_3CN and saturated with CO, was added to solid $NOBF_4$ (0.055 g, 0.47 mmol). The solution, which turned red brown, was stirred for 0.5 h. Ether was added, and the red-brown precipitate that formed was filtered off and discarded. More ether was added to the filtrate to give a white precipitate. Recrystallization of the white precipitate from CH_2Cl_2/Et_2O gave the desired product in 20% yield. ^1H NMR ($CDCl_3$): δ 3.4 (methylene, br), 6.8–8.0 (phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 5.2 (s). Anal. Calcd for $C_{53}H_{48}B_2BrF_8IrOP_4$: C, 50.10; H, 3.81. Found: C, 50.80; H, 3.68.

***trans*-[IrH(CO)(dppe)$_2$]X$_2$ (VII). Method A:** $[Ir(dppe)_2]Cl$ (1.09 g, 1.06 mmol) was dissolved in 5 mL of CH_2Cl_2 and the solution saturated with CO. HCl gas was then bubbled through the solution. Addition of THF precipitated *trans*-$[IrH(CO)(dppe)_2]Cl_2$ (VIIa),[13] which was filtered, washed with THF, and dried in vacuo. Metathesis with NH_4BF_4 and recrystallization from CH_2Cl_2/Et_2O gave *trans*-$[IrH(CO)(dppe)_2][BF_4]_2$ (VIIb) in 60% yield. ^1H NMR (CD_2Cl_2): δ −9.5 (hydride, q, J_{H-P} = 12.2 Hz), 3.0 (methylene, br), 6.7–7.5 (phenyl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 23.5 (s). Anal. Calcd for $C_{53}H_{49}B_2F_8IrOP_4$: C, 53.42; H, 4.14. Found: C, 54.17; H, 4.35.

Method B: $[Ir(dppe)_2]BF_4$ 1.26 g, 1.23 mmol) was dissolved in 10 mL of CH_2Cl_2. $HBF_4 \cdot Et_2O$ was added until the solution was no longer orange, and a slight excess was added. CO was then bubbled through the solution. Ether was added; *trans*-$[IrH(CO)(dppe)_2][BF_4]_2$ (VIIb) was filtered and recrystallized from CH_2Cl_2/THF; Isolated yield ca. 85%.

Reactions of *cis*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (IV) with Bases. (a) Pyridine. A sample of IV was dissolved in acetone, and an infrared spectrum showed absorptions for the starting material at 2135 and 2080 cm^{-1}. Pyridine was added to the solution. The vibrations at 2135 and 2080 cm^{-1} were replaced by a band for $Ir(CO)(dppe)_2^+$ (I) at 1950 cm^{-1}.

(b) Et_3N. Et_3N was added to a sample of IV dissolved in $CDCl_3$. A singlet at 25.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum showed the formation of $Ir(CO)(dppe)_2^+$ (I).

(c) NaOH. To a sample of IV dissolved in acetone was added an aqueous solution of NaOH. The solvent was removed, and $^{31}P\{^1H\}$ and ^1H NMR spectra of the resulting solid indicated that the product was $Ir(CO)(dppe)_2^+$ (I).

(d) H_2O. A sample of IV was dissolved in acetone-d_6 in an NMR tube. Peaks corresponding to IV in the $^{31}P\{^1H\}$ NMR spectrum disappeared on addition of H_2O to the sample. A new singlet for $Ir(CO)(dppe)_2^+$ (I), which appeared at 25.1 ppm, was slowly replaced by a singlet at 23.5 ppm corresponding to *trans*-$IrH(CO)(dppe)_2^{2+}$ (VII).

(e) Chloride. A sample of IV was dissolved in $CDCl_3$. Addition of tetrabutylammonium chloride afforded *trans*-$IrH(CO)(dppe)_2^{2+}$ (VII) and $IrHCl(dppe)_2^{2+}$, as evidenced by singlets in the $^{31}P\{^1H\}$ NMR spectrum at 23.5 and 21.0 ppm, respectively.

Electrochemical Oxidation of [Ir(CO)(dppe)$_2$]Cl. Electrochemical measurements and electrolyses were carried out on the following Princeton Applied Research equipment: Model 175 programmer, Model 173 potentiostat/galvanostat, Model 179 digital coulometer, and Model RE0074 XY recorder. Reported potentials are vs. Ag/AgI in 0.1 M tetrabutylammonium iodide in CH_3CN. The working electrode for cyclic voltammetry was a Pt disk.

Controlled-potential electrolyses were performed in a Metrohm cell with a cylindrical platinum-mesh electrode. The auxiliary electrode was a platinum spiral housed in a porous Vycor tube centrally located within the working electrode. The cell was flushed with N_2, and 50 mL of a 0.1 M solution of tetrabutylammonium chloride (TBAC) was syringed in. CO was bubbled through the solution throughout an electrolysis. A potential of +1.10 V was applied to the working electrode, and $[Ir(CO)(dppe)_2]Cl$ (0.103 g, 0.0977 mmol), dissolved in the electrolyte, was added. Electrolysis required 1.9 electrons per Ir.

Results

Synthesis and Characterization. *cis*-IrX(CO)(dppe)$_2^{2+}$ (X = Cl, Br, H). The reactions of $Ir(CO)(dppe)_2^+$ with the

(12) Vaska, L.; Catone, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 5324–5325.

(13) HCl_2^- may also be present as a counterion.

Table I. Infrared Spectral Data[a]

compd	ν(C≡O)	ν(Ir-H) or ν(Ir-Cl)
$[Ir(CO)(dppe)_2]BF_4$ (Ib)	1935	
cis-$[IrCl(CO)(dppe)_2][BF_4]_2$ (IIb)	2080	300
cis-$[IrBr(CO)(dppe)_2][BF_4]_2$ (IIIb)	2080	
cis-$[IrH(CO)(dppe)_2][BF_4]_2$ (IV)	2075	2140
trans-$[IrCl(CO)(dppe)_2][BF_4]_2$ (Vb)	2050	310
trans-$[IrBr(CO)(dppe)_2][BF_4]_2$ (VI)	2060	
trans-$[IrH(CO)(dppe)_2][BF_4]_2$ (VIIb)	2045	2160

[a] Nujol mulls; all values in cm^{-1}.

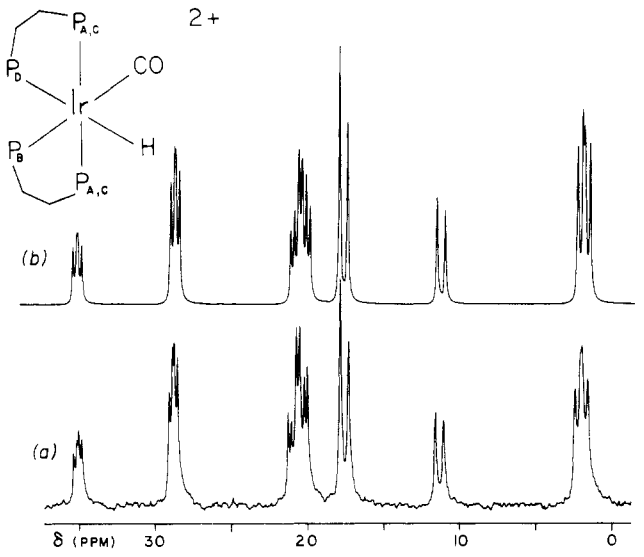
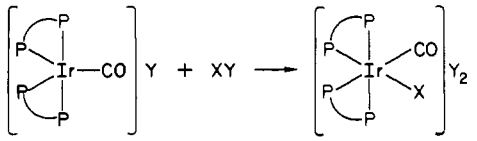


Figure 1. Observed (a) and calculated (b) $^{31}P\{^1H\}$ NMR spectra of *cis*-$[IrH(CO)(dppe)_2][BF_4]_2$.

inner-sphere oxidants X_2 (X = Cl, Br) and HBF_4 rapidly afford cis iridium(III) carbonyl dications according to eq 4.



(4)

I

IIa: X = Y = Cl
IIIa: X = Y = Br
IV: X = H, Y = BF_4

As will be shown subsequently, these products are kinetically formed. The trans isomers are not produced in eq 4, nor are they formed by isomerization of the cis isomers. Each of the cis complexes is stereochemically rigid, and none dissociates CO under ambient conditions. The cis carbonyl dications are soluble in polar solvents such as CH_2Cl_2, CH_3CN, and $MeNO_2$ but are insoluble in THF.

Compounds II–IV possess high C≡O stretching frequencies, 2075–2080 cm^{-1} (Table I), indicative of attenuated π bonding in these complexes. An Ir–Cl stretch for II is observed at 300 cm^{-1}. This value is at the high end of the range expected for a chloro ligand trans to phosphine in an octahedral Ir(III) complex.[14] The infrared spectrum of IV shows an Ir–H stretch at 2140 cm^{-1}.

$^{31}P\{^1H\}$ NMR spectra appear as ABMX patterns for these cis complexes owing to the magnetic inequivalence of the phosphorus atoms. A representative example is the spectrum of *cis*-$[IrH(CO)(dppe)_2][BF_4]_2$ (IV) shown in Figure 1. The large $J_{P-P(trans)}$ coupling constant of 228 Hz observed for IV is typical for these and other Ir(III) complexes, as are the

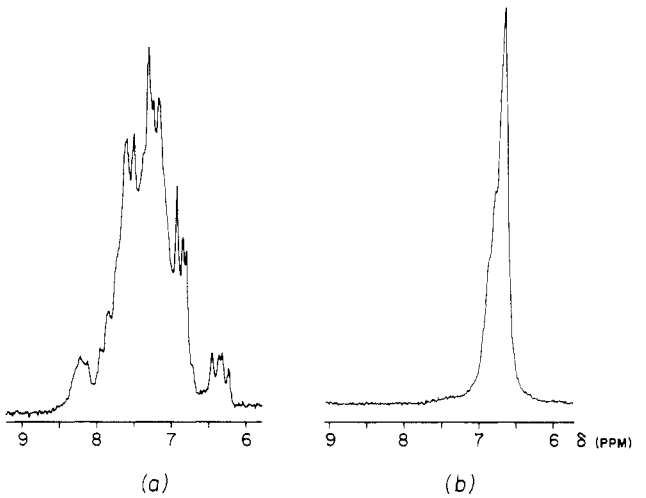
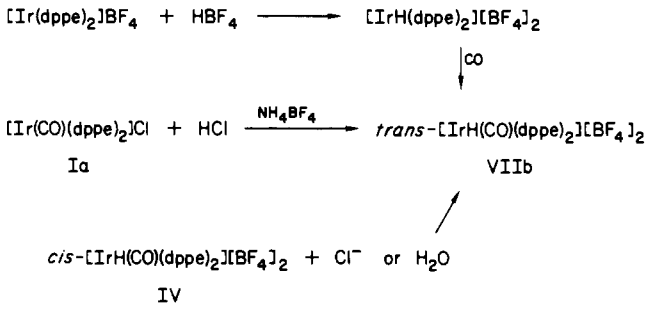


Figure 2. ^1H NMR spectra in the phenyl region: (a) *cis*-$[IrCl(CO)(dppe)_2][BF_4]_2$; (b) *trans*-$[IrCl(CO)(dppe)_2][BF_4]_2$.

Scheme I



$J_{P-P(cis)}$ values that fall in the range of 1.5–19.5 Hz.[15,16] The hydride resonance for IV appears in ^1H NMR spectra as a doublet of broad multiplets and is consistent with the assigned cis structure. The value of $J_{H-P(trans)}$ is 104 Hz, similar to the 113-Hz coupling observed in *cis*-$IrH_2(dppe)_2^+$.[17]

^1H NMR spectra in the phenyl region are much more complex for the cis isomers than for the trans isomers. Spectra for *cis*- and *trans*-$IrCl(CO)(dppe)_2^{2+}$ are compared in Figure 2. Important features in spectra of the cis compounds, which are absent in spectra of the trans compounds, are the doublets of doublets lying upfield from the major phenyl resonances. These features result from interaction of the phenyl ortho hydrogen atoms with the cis ligands; they have been seen previously in several other complexes of this type.[18,19] The doublet of doublet structure of the ortho hydrogen resonances in the spectra of these cis complexes arises from couplings with the phosphorus atom and the adjacent meta hydrogen atom.[18] Spectra of IV show two doublets of doublets centered at 6.49 and 6.13 ppm. For II, only one doublet of doublet is observed at 6.40 ppm. The other resonance is presumably buried under the main phenyl multiplet, as for *cis*-$RuCl(CH_3)(dppe)_2$.[12,18]

The ortho hydrogen-cis ligand interaction has been observed directly in the solid state. The crystal structure of *cis*-[Ir-

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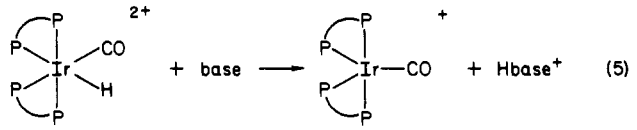
$(S_2)(dppe)_2]Cl$ clearly shows close ortho hydrogen–sulfur contacts calculated to be 2.57 and 2.54 Å.[20] The interacting phenyl groups are bonded to the phosphorus atoms lying in the equatorial plane.

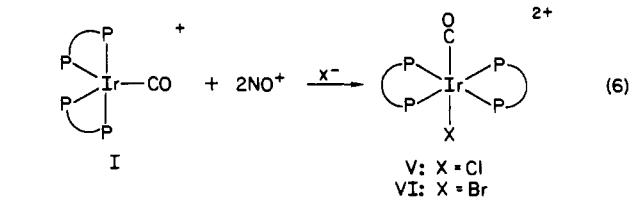
***trans*-IrH(CO)(dppe)$_2^{2+}$.** The complex *trans*-$[IrH(CO)(dppe)_2][BF_4]_2$ (VIIb) can be prepared by three routes, as outlined in Scheme I. The most convenient route involves protonation of $[Ir(dppe)_2]BF_4$ with $HBF_4 \cdot Et_2O$ to form the five-coordinate d^6 intermediate $[IrH(dppe)_2][BF_4]_2$. CO addition gives only the trans isomer (Scheme I). $[IrH(dppe)_2][BF_4]_2$ has also been prepared by an indirect route that involves protonation of $[Ir(dppe)_2]Cl$ with $HBF_4 \cdot Et_2O$ to afford $[IrHCl(dppe)_2]BF_4$ followed by abstraction of chloride with $AgBF_4$.[21]

In contrast to the reaction of HBF_4 with $[Ir(CO)(dppe)_2]BF_4$ (Ib) to yield *cis*-$IrH(CO)(dppe)_2^{2+}$ (IV), HCl reacts to afford *trans*-$IrH(CO)(dppe)_2^{2+}$ (VII) in variable yield along with $IrHCl(dppe)_2^{2+}$ (Scheme I). The effect of chloride on this protonation reaction was determined by the addition of tetrabutylammonium chloride to a solution of *cis*-$IrH(CO)(dppe)_2^{2+}$. Again, the isomerized products *trans*-$IrH(CO)(dppe)_2^{2+}$ and $IrHCl(dppe)_2^+$ are obtained. Water also slowly induces the isomerization of IV to VII, with $Ir(CO)(dppe)_2^+$ as an observed intermediate in this reaction (Scheme I). Deprotonation of *cis*-$IrH(CO)(dppe)_2^{2+}$ to afford $Ir(CO)(dppe)_2^+$ is irreversible with stronger bases such as pyridine, Et_3N, and OH^- (eq 5).



The assigned trans geometry for VII is consistent with the spectroscopic data. Strong vibrational coupling between C≡O and Ir—H stretching modes in the infrared region (Table I) results in an enhancement of the intensity of the Ir–H stretch. This enhancement is observed when hydride is trans to the CO ligand.[22] The $^{31}P\{^1H\}$ NMR spectrum shows a sharp singlet, and the hydride signal in the ^1H NMR spectrum appears as a quintet, indicating equivalent phosphorus atoms.[23]

***trans*-IrX(CO)(dppe)$_2^{2+}$ (X = Cl (V), Br (VI)).** The complexes *trans*-$IrX(CO)(dppe)_2^{2+}$ (X = Cl, Br) are prepared by oxidation of $Ir(CO)(dppe)_2^+$ with nitrosonium ion in the presence of Cl^- or Br^- (eq 6). The compound *trans*-$[IrCl(CO)(dppe)_2][BF_4]_2$ (Vb) is best prepared by the reaction of $[Ir(CO)(dppe)_2]Cl$ (Ia) and NOCl gas in CH_2Cl_2 followed by metathesis with NH_4BF_4. $NOBF_4$ reacts similarly; however, the substitution product $[Ir(NO)(dppe)_2][BF_4]_2$ is also formed in this reaction.[24] $NOBF_4$ is used to prepare the bromo derivative VI from $[Ir(CO)(dppe)_2]Br$.



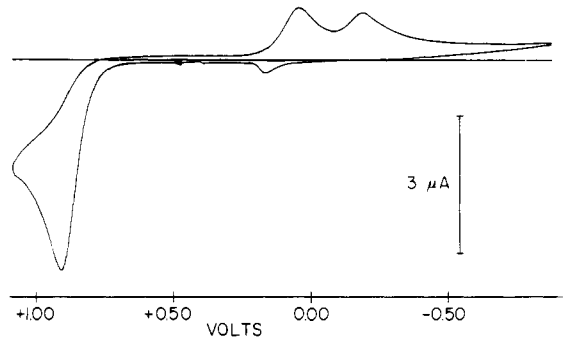


Figure 3. Cyclic voltammetry of $[Ir(CO)(dppe)_2]Cl$ in CH_2Cl_2 with 0.1 M TBAC as supporting electrolyte. The scan rate is 200 mV/s, and the reference electrode is Ag/AgI.

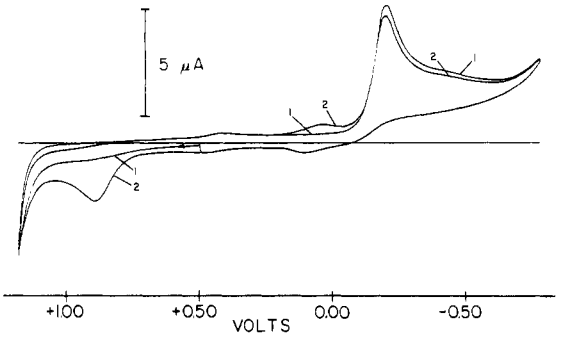


Figure 4. Two successive cyclic voltammograms of *trans*-$[IrCl(CO)(dppe)_2]Cl_2$ in CH_2Cl_2 with 0.1 M TBAC as supporting electrolyte. The scan rate is 200 mV/s, and the reference electrode is Ag/AgI.

Ferricinium tetrafluoroborate reacts with $[Ir(CO)(dppe)_2]Cl$ (Ia) to form *trans*-$[IrCl(CO)(dppe)_2][BF_4]_2$ (Vb). The reaction proceeds much more slowly than the NO^+ oxidation owing to the weaker oxidizing ability of $FeCp_2^+$.[25]

Infrared data for V and VI are listed in Table I. Carbonyl stretching frequencies are lower than for the cis isomers. The Ir–Cl stretching frequency for V occurs at 310 cm^{-1}, a value reasonable for chlorine trans to CO.[13] Phosphorus resonances appear as sharp singlets and are typical for the trans isomers.

Electrochemical Oxidation. Figure 3 shows a cyclic voltammogram for the oxidation of $Ir(CO)(dppe)_2^+$ in chloride media. As the potential is swept in the positive direction, a wave at +0.91 V corresponding to the oxidation of $Ir(CO)(dppe)_2^+$ occurs. Upon reversal of the sweep direction this wave is found to be irreversible, implying that a rapid follow-up chemical reaction has taken place. Two new irreversible waves with similar peak heights appear at +0.04 and −0.20 V as the cathodic scan continues. Controlled-potential electrolysis at +1.10 V shows that the oxidation is a two-electron process. $^{31}P\{^1H\}$ NMR spectra of the material obtained from the electrolyzed solution indicate that *cis*- and *trans*-$IrCl(CO)(dppe)_2^{2+}$ are the species formed (eq 7). Further electrochemical studies support the conclusion that the waves at

$$Ir(CO)(dppe)_2^+ + Cl^- \xrightarrow{-2e^-} cis/trans\text{-}IrCl(CO)(dppe)_2^{2+} \quad (7)$$

(20) Bonds, W. D., Jr.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 3413–3419.
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(23) The appearance of a quintet hydride resonance and a singlet phosphorus resonance do not always imply a trans geometry in these complexes. These features are seen in room-temperature spectra of $IrHCl(dppp)_2^+$.[16] The $^{31}P\{^1H\}$ NMR spectrum taken at −80 °C, however, shows an A_2X_2 pattern, indicating a cis structure in which the hydrogen and chlorine atoms undergo rapid site exchange. Spectra of $IrHCl(dppe)_2^+$ are temperature independent, showing quintet hydride and singlet phosphorus resonances. Although this could indicate a trans geometry, some have suggested that this complex is also fluxional, in analogy to $IrHCl(dppp)_2^+$.[16,21] Fluxionality in complex **VII** can clearly be ruled out since the cis isomer **IV** is readily isolated and shows no tendency to isomerize to **VII**.
(24) Haymore, B. L. Ph.D. Thesis, Northwestern University, 1975.
(25) Connelly, N. G.; Davies, J. D. *J. Organomet. Chem.* **1972**, *38*, 385–390.

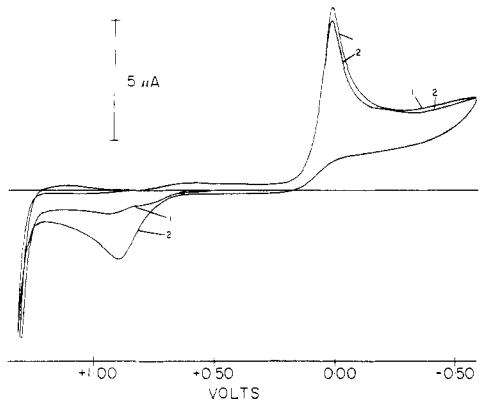


Figure 5. Two successive cyclic voltammograms of *cis*-[IrCl(CO)(dppe)$_2$]Cl$_2$ in CH_2Cl_2 with 0.1 M TBAC as supporting electrolyte. The scan rate is 200 mV/s, and the reference electrode is Ag/AgI.

+0.04 and −0.20 V result from reduction of *cis*-IrCl(CO)(dppe)$_2^{2+}$ and *trans*-IrCl(CO)(dppe)$_2^{2+}$, respectively. The trans isomer is reduced at a more negative potential and is therefore thermodynamically the more stable compound.

Two successive cyclic voltammograms of *trans*-[IrCl(CO)(dppe)$_2$]Cl$_2$ (Va) are shown in Figure 4. An anodic scan originating at +0.50 V shows that the solution is free of Ir(CO)(dppe)$_2^+$. The first cathodic scan shows only one wave at −0.21 V corresponding to the irreversible reduction of Va. Rescanning gives an irreversible oxidation wave at +0.91 V and a new irreversible reduction wave at +0.03 V along with the original peak at −0.21 V. Similar behavior is seen in successive cyclic voltammograms of *cis*-[IrCl(CO)(dppe)$_2$]Cl$_2$ (IIa) (Figure 5). Again, no oxidation waves are observed in an initial anodic scan. A single irreversible reduction wave appears at +0.03 V on the first cathodic scan and is assigned to the reduction of IIa. A new oxidation wave at +0.91 V, a new reduction wave at 0.20 V, and the original reduction wave at +0.03 V (all irreversible) appear upon rescanning. Reduction of both the cis and trans isomers results in the formation of [Ir(CO)(dppe)$_2$]Cl as indicated by the growth of the wave at +0.91 V (eq 8). Oxidation of [Ir(CO)(dppe)$_2$]Cl has already been shown to form a mixture of IIa and Va and thus accounts for the appearance of the new waves upon rescanning. Displacement of halide as a result of a two-electron reduction of a d^6 complex has been observed previously.[26]

$$cis/trans\text{-IrCl(CO)(dppe)}_2^{2+} \xrightarrow{+2e^-} \text{Ir(CO)(dppe)}_2^{+} + \text{Cl}^- \quad (8)$$

Discussion

Octahedral Ir(III) carbonyl dications are readily formed by oxidation of Ir(CO)(dppe)$_2^+$. Oxidation by halogens and HBF_4 affords the kinetic cis isomers while oxidation by NO^+ and $FeCp_2^+$ affords the thermodynamically more stable trans isomers. Electrochemical oxidation yields a mixture of the two.

Although Ir(CO)(dppe)$_2^+$ is in equilibrium with Ir(dppe)$_2^+$,[12,27] Ir(CO)(dppe)$_2^+$ is the complex oxidized to the observed products. Ir(dppe)$_2^+$ reacts with X_2,[12] NO^+,[24] and HX (X = halogen)[12] to form stable complexes that do not react with CO. *cis*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (IV) is formed by direct protonation of Ir(CO)(dppe)$_2^+$ since protonation of Ir(dppe)$_2^+$, followed by reaction with CO, affords only the trans isomer, *trans*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (VIIb).

The mode of formation of the cis isomers is that given in eq 2. Equation 3, i.e. displacement of a neutral ligand by counterion, does not take place under ambient conditions. For *cis*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$, Cl$^-$ does displace CO, but only as a side reaction. This is unusual since most cationic iridium and rhodium and isoelectronic iron, ruthenium, and osmium complexes lose CO or phosphine in the presence of halide.[5] The apparent lack of CO and phosphine lability in the complexes *cis*-IrX(CO)(dppe)$_2^{2+}$ (X = Cl (II), Br (III), H (IV)), which is also reflected by their configurational stability, is surprising since the CO and X ligands interact sterically with phenyl groups.

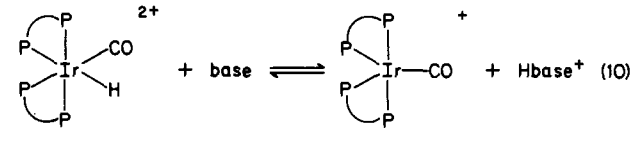
The reaction of Ir(CO)(dppe)$_2^+$ with NO^+ is dependent on counterion. In the presence of Cl$^-$ or Br$^-$, oxidation occurs to afford the trans halo carbonyl dications. When the counterion is BF_4^-, however, only substitution occurs (eq 9).[24]

$$[\text{Ir(CO)(dppe)}_2]\text{BF}_4 + \text{NOBF}_4 \rightarrow [\text{Ir(NO)(dppe)}_2][\text{BF}_4]_2 + \text{CO} \quad (9)$$

Halide ions therefore must assist in some manner with the electron transfer process. Since the overall oxidation is a two-electron process and since NO^+ is a one-electron oxidant, two successive electron-transfer steps are involved. Halide ions may help to stabilize the intermediate d^7 complex and promote the second electron transfer. Coordination of halide ion to the d^7 intermediate could also explain why only the trans isomer is formed, in contrast to the electrochemical oxidation in which a two-electron step results in the formation of both cis and trans isomers in approximately a 1:1 ratio.

Since the electrochemical oxidation of Ir(CO)(dppe)$_2^+$ gives a different product distribution from nitrosonium ion oxidation, even though both presumably are outer-sphere processes, different intermediates must be involved. The electrochemical oxidation, being a two-electron process, probably results in a five-coordinate d^6 Ir(III) species that rapidly adds chloride, either cis or trans, to the carbonyl ligand.

The oxidation of Ir(CO)(dppe)$_2^+$ by H^+ is also dependent on counterion. Thus, while HBF_4 affords *cis*-IrH(CO)(dppe)$_2^{2+}$ (IV), HCl forms a mixture of *trans*-IrH(CO)(dppe)$_2^{2+}$ (VII) and IrHCl(dppe)$_2^+$. We believe that *trans*-IrH(CO)(dppe)$_2^{2+}$ is formed in the HCl oxidation reaction by a chloride-induced isomerization of the kinetically formed protonation product, *cis*-IrH(CO)(dppe)$_2^{2+}$. This isomerization of IV to VII is independently observed when either Cl$^-$ or H_2O is added to a solution of IV. The intermediacy of Ir(CO)(dppe)$_2^+$ in the H_2O-induced isomerization suggests to us the importance of an equilibrium shown in eq 10. The



position of this equilibrium is dependent on base strength. Thus, for BF_4^-, a very weak base, the equilibrium lies completely to the left; IV is prepared in this manner. Stronger bases such as pyridine, Et_3N, and OH^- drive the reaction completely to the right.

Two equally likely pathways for the isomerization reaction in the presence of chloride, a base of intermediate strength, are shown in Scheme II. Common to both is the equilibrium shown in eq 10. Protonation of Ir(CO)(dppe)$_2^+$ may give an undetectable amount of *trans*-IrH(CO)(dppe)$_2^{2+}$ (VII). Since the hydrogen ligand in VII does not show acidic behavior, VII will accumulate at the expense of *cis*-IrH(CO)(dppe)$_2^{2+}$ (IV).

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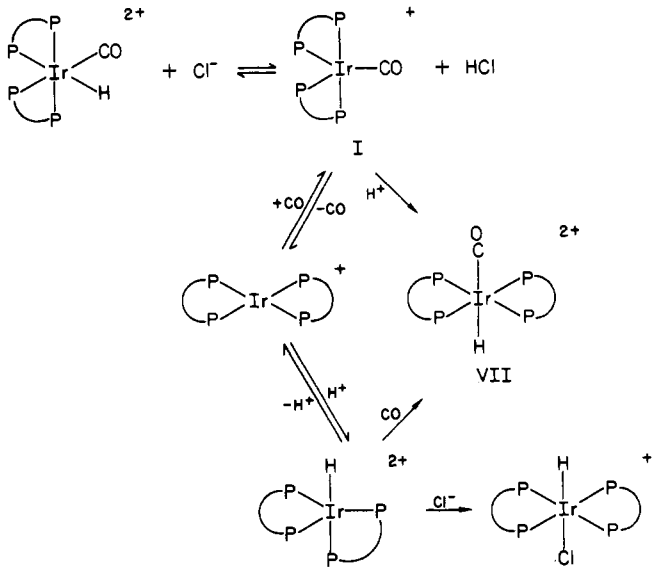
Scheme II



Alternatively, $Ir(dppe)_2^+$,[12,27] which is in equilibrium with $Ir(CO)(dppe)_2^+$, may undergo protonation to afford $IrH(dppe)_2^{2+}$. Subsequent reaction with CO affords VII. This pathway is used as a synthetic method to produce VII. The complex $IrHCl(dppe)_2^+$ could form by the known reaction of HCl with $Ir(dppe)_2^+$.[12,16]

The acidity of *cis*-$[IrH(CO)(dppe)_2][BF_4]_2$ is remarkable. Reversible deprotonation of this complex by chloride implies that its acidity is on the order of that of HCl. Although first-row transition-metal hydride complexes can show appreciable acidity,[28] this degree of acidity is unusual for complexes of the more basic third-row transition metals.[29,30] Hydrido transition-metal complexes of Ru,[31] Os,[8b,31] and Ir[32] have been depronated by strong bases such as alkoxide. The pK_a values for hydrido complexes of Os, W, Mo, and Cr are comparable with, or lower than, that of acetic acid.[29] The Brønsted acidity of *cis*-$[IrH(CO)(dppe)_2][BF_4]_2$ precludes activation of the coordinated CO to nucleophilic attack. Other members in the series of complexes *cis*- and *trans*-$IrX(CO)(dppe)_2^{2+}$ (X = Cl, H) are reactive with nucleophiles such as H_2O, OH^-, and H^- at the CO ligand. The results of these studies will be reported subsequently.[11]

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Registry No. Ia, 15308-58-4; Ib, 91685-28-8; IIa, 91606-09-6; IIb, 91606-11-0; IIIa, 91606-12-1; IIIb, 91606-14-3; IV, 91685-23-3; Va, 91685-24-4; Vb, 91685-25-5; VI, 91685-27-7; VIIa, 91606-15-4; VIIb, 66350-34-3; $[Ir(dppe)_2]Cl$, 15390-38-2; $[Ir(dppe)_2]BF_4$, 15130-28-6; $Ir_2Cl_2(C_8H_{24})_4$, 12246-51-4; $[Ir(CO)(dppe)_2]Br$, 15699-66-8.

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Immobile- and Mobile-Phase ESR Spectroscopy of Copper Complexes: Studies on Biologically Interesting Bis(thiosemicarbazonato)copper(II) Chelates

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Received April 19, 1984

ESR studies of an analogue of the antitumor agent [3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazonato)]copper(II), CuKTS, were undertaken to provide model data before studying the interaction of the analogues with Ehrlich cells. ESR data were taken at room temperature in anticipation of monitoring the fluidity of the environment about the copper complex. Room-temperature data vs. pH for [3-ethoxy-2-oxobutyraldehyde bis(N^4,N^4-dimethylthiosemicarbazonato)]copper(II), $CuKTSM_2$, clearly establish a low-pH and a high-pH form. Computer simulations of these spectra and spectra from published data are interpreted with use of a superposition of only these two distinct pH forms. The room-temperature ESR signal rapidly disappeared for CuKTS after incubation in Ehrlich ascites tumor cells and is consistent with previous reports of thiol reduction of CuKTS in Ehrlich cells. In contrast, the ESR signal for $CuKTSM_2$ was stable after incubation in Ehrlich cells and is consistent with the notion that CuKTS localizes in the cytoplasm and $CuKTSM_2$ localizes in the membrane. Surprisingly, $CuKTSM_2$ at low concentrations is essentially immobilized in its association with Ehrlich cells. This observation has not been previously made because only spectra for CuKTS in frozen samples of Ehrlich cells have been previously investigated.

Introduction

A number of copper complexes or ligands that bind copper have biological activity. Mono- and bis(thiosemicarbazonato)copper(II) complexes and analogues of the tripeptide H-Gly-His-Lys-OH have cytotoxic and antitumor effects.[3-7] In addition, copper(II) bleomycin has been extensively studied to determine its contribution to the antitumor activity of bleomycin.[8] The tripeptide H-Gly-His-Lys-OH and 2-formylpyridine thiosemicarbazone and derivatives, which respectively have hormonelike properties and antitumor

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