Me, 15%), and 139 mg of **26** (54%).

Photolysis of 7 in *tert*-Butyl Alcohol through a Filter Solution. A solution of **7** (300 mg, 0.681 mmol), *tert*-butyl alcohol (1 mL), and benzene (5 mL) was irradiated through a methanol solution of phenanthrene with a high-pressure mercury lamp for 13 h. Separation by HPLC followed by silica gel chromatography gave 33 mg of **23** (R = *t*-Bu, 13%), 33 mg of **25** (R = *t*-Bu, 13%), and 157 mg of **26** (68%).

Photolysis of 26 in *tert*-Butyl Alcohol. A solution of **26** (236 mg, 0.536 mmol), *tert*-butyl alcohol (1 mL), and benzene (5 mL) was irradiated through a Pyrex tube with a high-pressure mercury lamp for 12 h. Separation by HPLC followed by silica gel chromatography gave 33 mg of **23** (R = *t*-Bu, 13%), 49 mg of **25** (R = *t*-Bu, 19%), and recovered **26** (76 mg, 32%).

Thermolysis of 26 in *tert*-Butyl Alcohol. A solution of **26** (321 mg, 0.730 mmol), *tert*-butyl alcohol (2 mL), and benzene (4 mL) was heated in a sealed tube at 150 °C for 10 min. Separation by HPLC followed by silica gel chromatography gave 127 mg of **23** (R = *t*-Bu, 49%) and 81 mg of **25** (R = *t*-Bu, 31%).

Thermolysis of 26 in Methanol. A solution of **26** (235 mg, 0.534 mmol), methanol (2 mL), and benzene (4 mL) was heated in a sealed tube at 150 °C for 10 min. Separation by HPLC followed by silica gel chromatography gave 73 mg of **23** (R = Me, 22%), 70 mg of **24** (R = Me, 22%), and 135 mg of **25** (R = Me, 42%).

Thermolysis of 26 in 2,3-Dimethyl-1,3-butadiene. A solution of **26** (440 mg, 1.00 mmol) in 2,3-dimethyl-1,3-butadiene (5 mL) was heated in a sealed tube at 150 °C for 10 min. Separation by HPLC followed by silica gel chromatography (eluent carbon tetrachloride) gave **30** (70 mg, 14%): NMR (CCl_4, δ) 0.52 (s, 3 H, SiMe), 1.21 (s, 2 H, $SiCH_2C$), 1.64 (s, 3 H, C=CMe), 1.80 (s, 3 H, C=CMe), 2.01 (br t, 1 H, SiCH), 2.92 (br d, 2 H, $SiCCH_2$), 6.85–7.27 (m, 20 H, ArH); ^{13}C NMR ($CDCl_3$) −4.2 (q), 17.0 (t), 21.5 (q), 23.4 (q), 29.2 (d), 37.4 (t), 124.7, 124.9, 125.2, 125.5, 126.2, 126.6, 127.5, 127.6, 127.9, 128.1, 128.3, 128.4, 129.1, 129.8, 130.1 (s), 131.3 (s), 137.5 (s), 138.0 (s), 141.0 (s), 142.0 (s), 142.8 (s), 143.0 (s), 146.2 (s), 150.8 (s); IR (CCl_4) 1250 cm^{-1} (SiMe); mass spectrum, *m/e* 494 (M^+); high-resolution mass calcd for $C_{36}H_{34}Si$ 494.2427, found 494.2424.

Thermolysis of 26 in Benzophenone. A mixture of **26** (250 mg, 0.568 mmol) and benzophenone (750 mg, 4.12 mmol) was heated in a sealed tube at 150 °C for 10 min. Separation by HPLC followed by silica gel chromatography (eluent benzene) gave 1,1-diphenylpropene (15 mg, 14%) which was identified by comparison of its NMR and IR spectra with those of an authentic sample.

Photolysis of 8 in *tert*-Butyl Alcohol. A solution of **8** (300 mg, 0.660 mmol), *tert*-butyl alcohol (2 mL), and benzene (8 mL) was irradiated through a Pyrex tube with a high-pressure mercury lamp for 7 h. Separation by HPLC gave 156 mg of **31** (52%) and 75 mg of diazirine **32** (27%). Products **31** and **32** were identified by their NMR, IR, mass spectra, and elemental analyses.

Compound **31**, recrystallized from hexane: yellowish green crystals; mp 170–170.5 °C (lit.[20] mp 177–178 °C); NMR (CCl_4, δ) 0.58 (s, 3 H, SiMe), 5.76–6.60 (m, 3 H, $SiCH{=}CH_2$), 6.81–7.30 (m, 20 H, ArH); IR (KBr) 1250 cm^{-1} (SiMe); mass spectrum, *m/e* 426 (M^+). Anal. Calcd for $C_{31}H_{26}Si$: C, 87.27; H, 6.14. Found: C, 87.17; H, 6.14.

Compound **32**, recrystallized from pentane: yellowish green crystals; mp 142 °C dec; NMR (CCl_4, δ) 0.21 (s, 3 H, SiMe), 0.91 (s, 3 H, CN_2Me), 6.76–7.36 (m, 20 H, ArH); IR (KBr) 1610 cm^{-1} (N=N); mass spectrum, *m/e* 426 ($M^+ - 28$); ^{13}C NMR ($CDCl_3$) 7.5 (q), 15.6 (s), 18.4 (q), 125.6 (d), 126.1 (d), 126.3 (d), 126.6 (d), 127.6 (d), 127.9 (d), 128.2 (d), 129.1 (d), 129.8 (d), 130.0 (d), 137.3 (s), 138.4 (s), 138.7 (s), 156.6 (s) ppm. Anal. Calcd for $C_{31}H_{26}N_2Si$: C, 81.89; H, 5.76; N, 6.16. Found: C, 82.08; H, 5.80; N, 5.95.

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Registry No. **4**, 77999-12-3; **5**, 77999-16-7; **6**, 82644-70-0; **7**, 89175-80-4; **7** (lithium salt), 94671-27-9; **8**, 94671-28-0; **12**, 77999-13-4; **14**, 15570-45-3; **14-d_2**, 77999-14-5; **15a**, 77999-15-6; **15b**, 6937-59-3; **16**, 77999-17-8; **21**, 21993-93-1; **22**, 94671-29-1; **23** (R = Me), 89175-85-9; **23** (R = *t*-Bu), 89175-82-6; **23-d_1** (R = Me), 94671-30-4; **24** (R = Me), 89175-83-7; **24-d_1** (R = Me), 94671-31-5; **25** (R = Me), 89175-86-0; **25** (R = *t*-Bu), 89175-84-8; **25-d_1** (R = Me), 94671-32-6; **26**, 89175-81-5; **30**, 89175-87-1; **31**, 51528-39-3; **32**, 94671-33-7; $Ph_2P(O)N_3$, 26386-88-9; 1-methyl-1-(chloromethyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene, 94671-34-8; 1,1-diphenylpropene, 778-66-5; 2,3-dimethyl-1,3-butadiene, 513-81-5.

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Carbon Monoxide Activation by Iridium(III) Dicationic Carbonyl Complexes

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The cationic *cis*- and *trans*-$IrX(CO)(dppe)_2^{2+}$ (X = H, Cl) species react with nucleophiles, such as H_2O, OH^-, and H^-, to afford hydroxycarbonyl and formyl cations of Ir(III) typified by the species *trans*-$IrH(COOH)(dppe)_2^+$ and *trans*-$IrX(CHO)(dppe)_2^+$. The formyl complexes are protonated by strong acids to afford the electrophilic dicationic hydroxycarbene complexes *trans*-$IrX(CHOH)(dppe)_2^{2+}$. Reactivities and stabilities of these species are discussed.

Introduction

The reactions of coordinated carbon monoxide have long been a topic of interest because of the involvement of carbon monoxide in a variety of organotransition-metal-catalyzed reactions in which useful organic molecules are synthesized.[1,2] Catalysis of carbon monoxide hydrogenation[3] and the water gas shift reaction[4-10] are two areas that have received considerable attention. Modeling of species thought to be intermediates in these processes[11-13] has been

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Table I. Infrared Spectral Data for Selected Compounds[a]

	compound	ν(C=O)	ν(Ir—H) or ν(Ir—Cl)	other
II	*trans*-[IrCl(CO_2Me)(dppe)$_2$][BF_4]	1640	270	
VII	*trans*-[IrH(CO_2H)(dppe)$_2$][BF_4]	1610	2080	ν(OH) 3435[b]
VIIIa	*trans*-[IrCl(CHO)(dppe)$_2$][BF_4]	1625	220	ν(CH) 2660[c]
IXa	*trans*-[IrH(CHO)(dppe)$_2$][BF_4]	1590	1940	ν(CH) 2560[d]
X	*trans*-[IrH(CHOH)(dppe)$_2$][BF_4]$_2$		2040	

[a] Nujol mulls; all values in cm^{-1}. [b] CH_2Cl_2 solution. [c] *trans*-[IrCl(CDO)(dppe)$_2$][BF_4] (VIIIb): ν(CD) 2015 cm^{-1} (ν(CH)/ν(CD) 1.32). [d] *trans*-[IrH(CDO)(dppe)$_2$][BF_4] (IXb): ν(CD) 1920 cm^{-1} (ν(CH)/ν(CD) = 1.33).

vigorously pursued in order to delineate basic modes of reactivity.[14-32]

In a previous report we described the oxidation of Ir(CO)(dppe)$_2^+$ to afford a series of Ir(III) dicationic carbonyl complexes of the type *cis*- and *trans*-IrX(CO)(dppe)$_2^{2+}$ (X = H, Cl).[33,34] Here we describe the reactivity of these complexes with nucleophiles such as H_2O, OH^-, and H^-. In addition to the hydroxycarbonyl complex IrH(COOH)(dppe)$_2^+$ and the cationic formyl complexes IrX(CHO)(dppe)$_2^+$ (X = H, Cl), we describe the preparation and characterization of the electrophilic hydroxycarbene complex IrH(CHOH)(dppe)$_2^{2+}$, the second such species to be isolated. Conclusions are drawn regarding the steric and electronic factors involved in the stabilization of hydroxycarbene, formyl, and hydroxycarbonyl species.

Experimental Section

All manipulations were carried out under prepurified dinitrogen with the use of standard Schlenk-line procedures. Solvents were purified by standard methods. $LiBEt_3H$, $LiBEt_3D$, and LiB(*sec*-Bu)$_3$H were obtained from Aldrich Chemical Co. and used as received.

Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer for samples prepared as Nujol mulls, unless otherwise noted. Spectral results are presented in Table I. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL FX90Q spectrometer. Positive ^{31}P chemical shifts are downfield of 85% H_3PO_4 external standard. Elemental analyses were conducted by Micro-Tech Laboratories, Inc., Skokie, IL, and by Schwarzkopf Laboratories, Woodside, NY.

Syntheses. The complexes *cis*-[IrCl(CO)(dppe)$_2$][BF_4]$_2$[33] (I), *trans*-[IrCl(CO)(dppe)$_2$][BF_4]$_2$[33] (IIIa), [IrHCl(dppe)$_2$][BF_4][35] (IV), *cis*-[IrH(CO)(dppe)$_2$][BF_4]$_2$[33] (V), and *trans*-[IrH(CO)(dppe)$_2$][BF_4]$_2$[33] (VI) were prepared as previously described.

***trans*-[IrCl(CO_2Me)(dppe)$_2$][BF_4] (II).** The complex *cis*-[IrCl(CO)(dppe)$_2$][BF_4]$_2$ (I) (0.200 g, 0.163 mmol) was dissolved in 20 mL of CH_2Cl_2. Three milliliters of a freshly prepared NaOMe solution in MeOH (0.0631 M, 0.189 mmol) was added, and the solution was stirred for 10 min. The solvent was removed under vacuum and 15 mL of CH_2Cl_2 was added to the residue. A white solid was filtered, washed, and discarded. The solvent was again removed, and the product was recrystallized from THF/Et_2O to afford colorless crystals: ^1H NMR ($CDCl_3$) δ 2.54 (methyl, s), 2.99 (methylene, br), 7.17 (phenyl); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 1.9 (s). Anal. Calcd for $C_{58}H_{59}BClF_4IrO_3P_4$ (sample shown to contain ca. 1 equiv of Et_2O by ^1H NMR spectroscopy): C, 55.98; H, 4.94. Found: C, 55.89; H, 4.75.

***trans*-[IrCl(CO)(dppe)$_2$][SO_3CF_3]$_2$ (IIIb).** The complex *trans*-[IrCl(CO)(dppe)$_2$][SO_3CF_3]$_2$ (IIIb) was prepared in a manner analogous to that used to prepare the BF_4^- salt IIIa[33] described previously. Metathesis of *trans*-[IrCl(CO)(dppe)$_2$]Cl_2 was carried out in CH_2Cl_2 by addition of 2 equiv of Ag[SO_3CF_3] dissolved in acetone. The solution was filtered and a residue obtained by removal of the solvents from the filtrate. The residue was recrystallized from CH_2Cl_2/THF to afford the desired product.

***trans*-[IrH(CO_2H)(dppe)$_2$][BF_4] (VII).** A solution of *trans*-[IrH(CO)(dppe)$_2$][BF_4] (VI) (0.184 g, 0.169 mmol) in CH_3CN was treated with 1 equiv of an aqueous 0.197 M NaOH solution (0.87 mL, 0.17 mmol). The solvent was removed after ca. 0.5 h, and 5 mL of CH_2Cl_2 was added. A solid was filtered, washed, and discarded. The volume of the filtrate was reduced to ca. 3 mL, and Et_2O was added slowly. A white precipitate that formed was

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identified as unreacted starting material. The remaining material was a mixture of VII and the deprotonation product $Ir(CO)(dppe)_2^+$. The two products could not be separated by recrystallization. The reaction of OH^- with VI in acetone also gave VII. However, decomposition occurred in this solvent to form $IrH_2(dppe)_2^+$: ^1H NMR (CD_3CN) δ −13.5 (hydride, q, $J_{hydride-P}$ = 15.2 Hz), 2.9 (methylene, br), 7.4 (phenyl); $^{31}P\{^1H\}$ NMR (CD_3CN) δ 25.2 (s). A resonance for the hydroxyl proton was not observed in the ^1H NMR spectrum.

***trans*-[IrCl(CHO)(dppe)$_2$][BF$_4$] (VIIIa).** CH_2Cl_2 (5 mL) was added to *trans*-$[IrCl(CO)(dppe)_2][BF_4]_2$ (IIIa) (0.257 g, 0.226 mmol) and the mixture cooled to −78 °C. $LiB(sec\text{-}Bu)_3H$ (0.70 mL, 0.70 mmol) was added. The mixture was stirred at −78 °C for 0.5 h and allowed to warm slowly to room temperature to dissolve the suspended solid. Addition of ether gave a precipitate. Recrystallization at −78 °C invariably gave a product containing the decomposition product $[IrHCl(dppe)_2][BF_4]$: ^1H NMR (CD_2Cl_2, −50 °C) δ 3.0 (methylene, br), 6.5–8.0 (phenyl), 11.4 (formyl, q, $J_{formyl-P}$ = 6.6 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C) δ 16.3 (s).

The same method was used to prepare the deuterated formyl complex *trans*-$[IrCl(CDO)(dppe)_2][BF_4]$ (VIIIb) with the use of $LiBEt_3D$ in place of $LiB(sec\text{-}Bu)_3H$: ^1H NMR (CD_2Cl_2, −50 °C) δ 3.0 (methylene, br), 6.5–8.0 (phenyl); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C) δ 16.3 (s).

***trans*-[IrH(CHO)(dppe)$_2$][BF$_4$] (IXa).** The compound *trans*-$[IrH(CO)(dppe)_2][BF_4]_2$ (VI) (0.711 g, 0.596 mmol) was dissolved in 5 mL of CH_2Cl_2 and was cooled to −45 °C. $LiB(sec\text{-}Bu)_3H$ (1.8 mL, 1.8 mmol) was added, and the solution was stirred for 5 h. The solvent was removed under vacuum at −30 °C, and the residue was recrystallized from acetonitrile/ether at room temperature to afford the desired product: yield 75%, ^1H NMR (acetone-d_6) δ −13.6 (hydride, dq, $J_{hydride-formyl}$ = 9.8 Hz, $J_{hydride-P}$ = 15.3 Hz), 2.5 (methylene, br), 6.5–8.2 (phenyl), 14.4 (formyl, br m); $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 28.9 (s). Anal. Calcd for $C_{53}H_{50}BF_4IrOP_4$: C, 57.56; H, 4.56. Found: C, 57.44; H, 4.59.

The same method was used to prepare the deuterated formyl complex *trans*-$[IrH(CDO)(dppe)_2][BF_4]$ (IXb) with the use of $LiBEt_3D$ in place of $LiB(sec\text{-}Bu)_3H$: ^1H NMR (acetone-d_6) δ −13.6 (hydride, q, $J_{hydride-P}$ = 15 Hz), 2.5 (methylene, br), 6.5–8.2 (phenyl); $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 28.9 (s).

***trans*-IrH(CHOH)(dppe)$_2$][BF$_4$]$_2$ (X). (a) In situ.** At −50 °C *trans*-$[IrH(CHO)(dppe)_2][BF_4]$ (IXa) was dissolved in $CDCl_3$. A slight excess of $HBF_4{\cdot}Et_2O$ was added, and the sample was placed in an NMR probe at −50 °C. $^{31}P\{^1H\}$ NMR spectra show a new singlet at 28.7 ppm. A new hydride resonance appears as a broad multiplet in the ^1H NMR spectrum at −11.6 ppm. Low-field resonances are present at 13.1 (*CH*OH, br m) and 16.0 ppm (CHO*H*, br d, $J_{CHOH-CHOH}$ = 8.5 Hz). Decoupling at 13.1 ppm results in the collapse of the −11.6 ppm resonance to a quintet ($J_{hydride-P}$ = 14.6 Hz) and of the 16.0 ppm resonance to a broad singlet.

(b) Isolation as the Ethyl Ether Adduct [IrH(CHOH)(OEt$_2$)(dppe)$_2$][BF$_4$]$_2$. The complex *trans*-$[IrH(CHO)(dppe)_2][BF_4]$ (IXa) (ca. 0.40 g, 0.36 mmol) was cooled to −78 °C, and 5 mL of CH_2Cl_2 was slowly added. Excess $HBF_4{\cdot}Et_2O$ was added, and the solution was stirred for 10 min. Addition of Et_2O resulted in the precipitation of a white solid that was filtered, washed with Et_2O, and pumped dry. Recrystallization from CH_2Cl_2/THF at room temperature gave the desired product: ^1H NMR (CD_3CN, +30 °C) (Figure 1) δ −12.1 (hydride, qd, $J_{CHOH-hydride}$ = 7.3 Hz, $J_{hydride-P}$ = 14.6 Hz), 1.2 (methyl, t, J_{H-H} = 7.1 Hz), 2.9 (methylene, br m), 4.5 (methylene, qu, J_{H-H} = 7.1 Hz), 6.5–7.5 (phenyl), 12.8 (*CH*OH, br s) (decoupling the 12.8 ppm resonance results in collapse of the −12.1 ppm resonance to a quintet ($J_{hydride-P}$ = 14.6 Hz)); $^{31}P\{^1H\}$ NMR (CD_3CN, +30 °C) δ 28.7 (s). Anal. Calcd for $C_{57}H_{61}B_2F_8IrO_2P_4$: C, 53.58; H, 4.81. Found: C, 53.38; H, 4.69.

Reaction of *cis*-[IrCl(CO)(dppe)$_2$][BF$_4$]$_2$ (I) with MeOH in the Presence of Et$_3$N. To a solution of I in CD_2Cl_2 were added MeOH and Et_3N. Peaks in the $^{31}P\{^1H\}$ NMR spectrum corresponding to I decreased and were replaced after ca. 0.5 h by a singlet for *trans*-$[IrCl(CO_2Me)(dppe)_2][BF_4]$ (II) at 2.2 ppm.

Reaction of *trans*-[IrCl(CO$_2$Me)(dppe)$_2$][BF$_4$] (II) with Acid. HCl gas was bubbled through a solution of II in $CDCl_3$. $^{31}P\{^1H\}$ NMR spectra show the disappearance of the singlet at 1.9 ppm for II and the appearance of a peak at 11.2 ppm for *trans*-$[IrCl(CO)(dppe)_2]^{2+}$ (III).

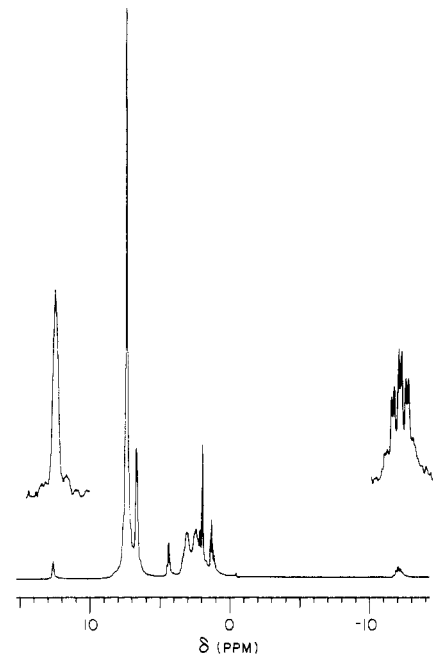


Figure 1. ^1H NMR spectrum of *trans*-$[IrH(CHOH)(O(C_2H_5)_2)(dppe)_2][BF_4]_2$ in CD_3CN.

Reaction of *cis*-[IrCl(CO)(dppe)$_2$][BF$_4$]$_2$ (I) with H$_2$O. When water was added to an acetone suspension of I, immediate dissolution of the solid occurred. An infrared spectrum of the solution (BaF_2 solution cells) showed a CO_2 vibration at 2320 cm^{-1}. The solvent was then removed under vacuum. Infrared and NMR spectra of the resulting solid were identical with spectra of an independently prepared sample of $[IrHCl(dppe)_2][BF_4]$ (IV).[35]

In an NMR experiment, ca. 20 mg of I was dissolved in 2:1 acetone-d_6/water at −30 °C. Initiation of a reaction to form IV occurred on warming the sample to −15 °C. No intermediates were detected.

Reaction of *cis*-[IrCl(CO)(dppe)$_2$][BF$_4$]$_2$ (I) with OH$^-$. In an NMR tube at −40 °C ca. 20 mg of I was dissolved in 2:1 acetone-d_6/H_2O. When a solution of NaOH in water was added, an immediate color change to orange occurred. A singlet at +50.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum shows the formation of $Ir(dppe)_2^+$.

Attempted Reaction of [IrHCl(dppe)$_2$][BF$_4$] (IV) with OH$^-$. This experiment was carried out in exactly the same manner as for the reaction of I with OH^-. No reaction took place.

Attempted Reaction of *trans*-[IrCl(CO)(dppe)$_2$][SO$_3$CF$_3$]$_2$ (IIIb) with H$_2$O. A solution of *trans*-$[IrCl(CO)(dppe)_2][SO_3CF_3]_2$ (IIIb) dissolved in 5:1 acetone/water was refluxed under N_2 for 6 h. The solvent was pumped off under vacuum, and the resulting solid was redissolved in $CDCl_3$. A $^{31}P\{^1H\}$ NMR spectrum indicated that no reaction had taken place. The $CDCl_3$ was removed, the residue was redissolved in 5:1 acetonitrile/water, and the solution was refluxed for an additional 7 h. The $^{31}P\{^1H\}$ NMR spectrum again showed only starting material.

Reaction of *trans*-[IrCl(CO)(dppe)$_2$][SO$_3$CF$_3$]$_2$ (IIIb) with OH$^-$. Approximately 20 mg of IIIb was dissolved in 2 mL of CD_3CN, and the solution was cooled to −20 °C. Addition of an aqueous NaOH solution afforded $Ir(dppe)_2^+$, as evidenced by a singlet at +50.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Similar results were found in a acetone-d_6/water solution at −40 °C.

Attempted Reaction of *trans*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (VI) with H$_2$O. A solution of VI dissolved in 5:1 acetone/water was refluxed for 6 h. An orange solution resulted. The solvent was pumped off under vacuum, and the residue was dissolved in $CDCl_3$. The $^{31}P\{^1H\}$ NMR spectrum indicated the presence of $IrH(dppe)_2^{2+}$ [33,35] (31.1 ppm (br s)) and $Ir(dppe)_2^+$ (+50.0 ppm (s)). In a similar experiment VI was again dissolved in 5:1 acetone/water. With a slow CO purge the solution was refluxed for 7 h and remained colorless. NMR spectra show only unreacted VI.

Reaction of *cis*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (V) with H$_2$O. A sample of V was dissolved in acetone-d_6 in an NMR tube. Peaks corresponding to V in the $^{31}P\{^1H\}$ NMR spectrum disappeared on addition of H_2O to the sample. A new singlet for Ir(CO)(dppe)$_2^+$ that appeared at 25.1 ppm was slowly replaced by a singlet at 23.5 ppm corresponding to *trans*-IrH(CO)(dppe)$_2^{2+}$ (VI).

Reaction of *cis*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (V) with OH$^-$. To a sample of V dissolved in acetone was added an aqueous solution of NaOH. The solvent was removed. Subsequent $^{31}P\{^1H\}$ and ^1H NMR spectroscopy on the product identified it as [Ir(CO)(dppe)$_2$][BF$_4$].

Reaction of *trans*-[IrH(CO$_2$H)(dppe)$_2$][BF$_4$] (VII) with Acid. To a sample of VII, prepared in situ by addition of an aqueous NaOH solution to *trans*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (VI) dissolved in CD_3CN, was added $HBF_4{\cdot}Et_2O$. $^{31}P\{^1H\}$ and ^1H NMR spectra showed the formation of *trans*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (VI). Addition of ether to the reaction mixture precipitated a solid that had bands in the infrared spectrum at 2050 and 2160 cm^{-1}, identical with bands assigned to ν(C≡O) and ν(Ir—H) in the infrared spectrum of VI.

Reaction of *cis*-[IrCl(CO)(dppe)$_2$][BF$_4$]$_2$ (I) with LiBEt$_3$H. Approximately 20 mg of I was dissolved in CD_2Cl_2 in an NMR tube, and the solution was cooled to −78 °C. $LiBEt_3H$ (ca. twofold excess) was added, and the NMR tube was placed in the precooled probe at −70 °C. $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded at this temperature and at 10 °C intervals on warming. ^1H NMR spectra from −70 to −30 °C show a formyl resonance appearing as a doublet of multiplets centered at 12.9 ppm. $^{31}P\{^1H\}$ NMR spectra in this temperature range are temperature dependent. Broad featureless resonances at −70 °C coalesce at ca. −60 °C and begin to sharpen at higher temperatures. The resonances are not fully resolved at −20 °C where decomposition occurs at an appreciable rate. The major decomposition product at −20 °C (with excess $LiBEt_3H$) is Ir(CO)(dppe)$_2^+$, as indicated by a singlet at 24.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum. As the temperature is raised further this peak is replaced by triplets at 31.5 and 20.0 ppm (J_{P-P} = 7.9 Hz) that arise from *cis*-IrH$_2$(dppe)$_2^+$. Hence H_2 is liberated in the decomposition process. A peak in the $^{31}P\{^1H\}$ NMR spectrum at 15.9 ppm at −30 °C shifts to 16.3 ppm at +30 °C and is assigned to *trans*-IrCl(CHO)(dppe)$_2^+$ (VIIIa).

Reaction of *cis*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (V) with LiB(*sec*-Bu)$_3$H. A solution of V in CD_2Cl_2 was cooled to −50 °C and LiB(*sec*-Bu)$_3$H was added. A reaction took place slowly to form Ir(CO)(dppe)$_2^+$, as evidenced by a broad singlet at 24.5 ppm. As the solution was warmed, this peak sharpened and moved to 25.0 ppm. No evidence for a formyl resonance was found in the ^1H NMR spectra.

Reaction of *trans*-[IrH(CHOH)(dppe)$_2$][BF$_4$]$_2$ (X) with Et$_3$N. To a solution of *trans*-[IrH(CHOH)(dppe)$_2$][BF$_4$]$_2$ (X) in CD_3CN were added several drops of Et_3N. New resonances at 28.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum and at −13.7 and 14.2 ppm in the ^1H NMR spectrum demonstrate the formation of *trans*-[IrH(CHO)(dppe)$_2$][BF$_4$] (IXa).

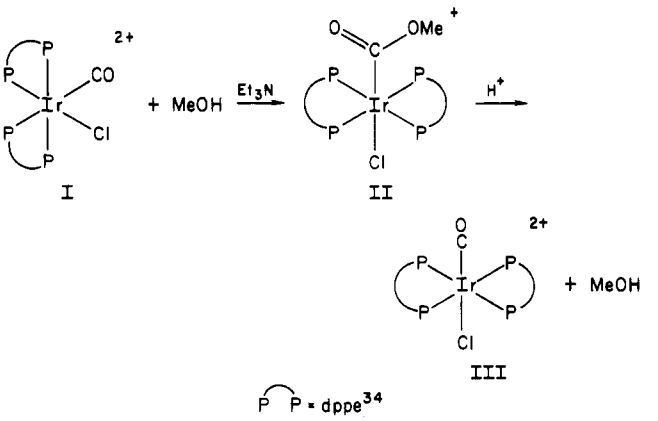
Reaction of *trans*-[IrCl(CHO)(dppe)$_2$][BF$_4$] (VIIIa) with HBF$_4{\cdot}$Et$_2$O. Approximately 20 mg of VIIIa was dissolved in $CDCl_3$ at −50 °C. Slightly less than 1 equiv of $HBF_4{\cdot}Et_2O$ was added, and the sample was placed in an NMR probe at −50 °C. A new singlet appeared at 11.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum. A broad resonance in the ^1H NMR spectrum occurred at 12.5 ppm. No other new low field or hydride resonances were present. When the sample was warmed to +30 °C, decomposition of the product resulted with *cis*-[IrH(CO)(dppe)$_2$][BF$_4$]$_2$ (V) precipitating from the solution, as evidenced by the $^{31}P\{^1H\}$ NMR spectrum and by vibrations in the infrared spectrum at 2135 and 2070 cm^{-1}.

Isolation of the hydroxycarbene complex was attempted at low temperature. Ten milliliters of CH_2Cl_2 was added slowly to dissolve solid VIIIa cooled to −78 °C. Several drops of $HBF_4{\cdot}Et_2O$ were added to the stirred solution. Slow addition of 25 mL of Et_2O precipitated a white solid. The solid was filtered cold and pumped dry under vacuum. NMR spectra of a sample of this material dissolved in $CDCl_3$ at −50 °C show resonances only for complex VIIIa.

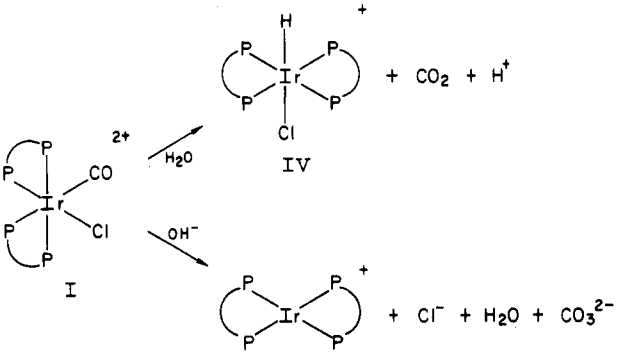
Results

Reaction of *cis*-IrCl(CO)(dppe)$_2^{2+}$ with Methanol and Methoxide. The complex *cis*-IrCl(CO)(dppe)$_2^{2+}$ (I) is susceptible to attack at the carbonyl carbon atom by weak nucleophiles. This reactivity is demonstrated by the reaction of I with methanol in the presence of triethylamine to afford the trans methoxycarbonyl complex II (Scheme I). This reaction, monitored by $^{31}P\{^1H\}$ NMR spectroscopy, is complete in approximately 30 min and only the trans isomer is formed. Complex II may also be prepared by the reaction of I with MeO$^-$. Typical of alkoxycarbonyl complexes is the reaction of II with acid to form the carbonyl complex *trans*-IrCl(CO)(dppe)$_2^{2+}$, III[19,36] (Scheme I).

Scheme I



Scheme II



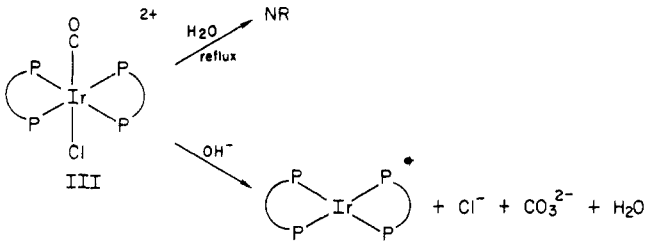
Reactivity of the Complexes *cis*- and *trans*-IrX(CO)(dppe)$_2^{2+}$ (X = Cl, H) with Water and Hydroxide. (i) *cis*-IrCl(CO)(dppe)$_2^{2+}$. Among this series of complexes *cis*-[IrCl(CO)(dppe)$_2$][BF$_4$]$_2$ (I) is the most reactive with water. At room temperature it reacts to form [IrHCl(dppe)$_2$][BF$_4$] (IV) (Scheme II). The liberation of CO_2 is verified by the growth of a band at 2320 cm^{-1} in solution infrared spectra taken during the course of the reaction. Variable-temperature NMR studies indicate that the reaction of I with H_2O takes place at temperatures as low as −15 °C.

The reaction of I with NaOH at low temperature was monitored by NMR spectroscopy. An immediate reaction occurs upon mixing I and OH$^-$ at −50 °C; the resultant bright orange solution contains Ir(dppe)$_2^+$, as indicated by a singlet at +50.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum (Scheme II). No intermediates were detected in this reaction.

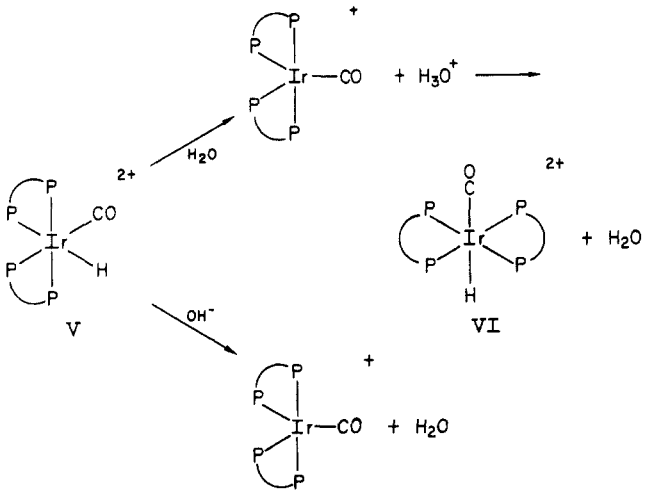
(ii) *trans*-IrCl(CO)(dppe)$_2^{2+}$. The complex *trans*-[IrCl(CO)(dppe)$_2$][SO$_3$CF$_3$]$_2$ (IIIb), unlike the cis isomer I, is resistant to nucleophilic attack by water. Complex IIIb was unchanged after 6 h of refluxing in an acetone/

(36) (a) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A.* **1969**, *443*–446. (b) Malatesta, L.; Caglio, G.; Angoletta, M. *J. Chem. Soc.* **1965**, *6974*–6983. (c) Ibekwe, S. D.; Taylor, K. A. *J. Chem. Soc. A* **1970**, 1–3. (d) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335–341.

Scheme III



Scheme IV



water solution and after an additional 7 h of refluxing in an acetonitrile/water solution. Complex IIIb did react with hydroxide ion in a manner analogous to I, however. Addition of hydroxide ion to IIIb resulted in the formation of $Ir(dppe)_2^+$ with no detectable intermediates. Scheme III summarizes these results.

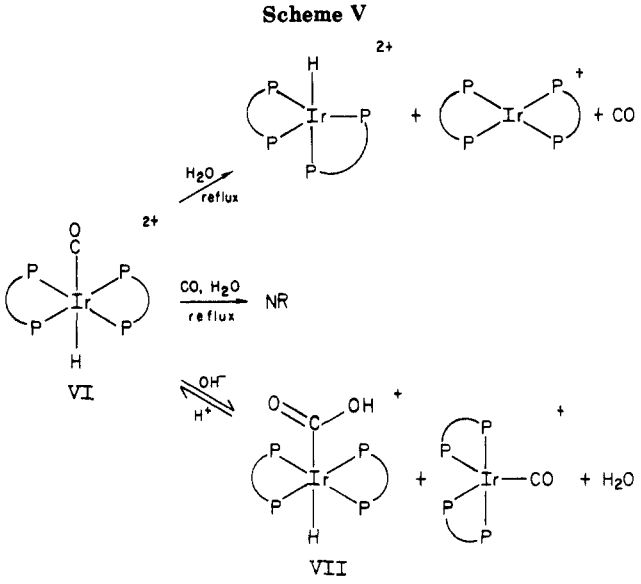
(iii) *cis*-IrH(CO)(dppe)$_2^{2+}$. In an earlier report we described the reactions of water and hydroxide ion with *cis*-$IrH(CO)(dppe)_2^{2+}$ (V).[33] This complex was expected to show reactivity with water similar to *cis*-$IrCl(CO)(dppe)_2^{2+}$ (I): both complexes have the same cis geometry and have similar $\nu(C{\equiv}O)$ stretching frequencies (I, $\nu(C{\equiv}O)$ 2080 cm^{-1}; V, $\nu(C{\equiv}O)$ 2075 cm^{-1}). Unexpectedly, nucleophilic attack at CO does not occur in the reaction of V with H_2O, but rather isomerization to *trans*-$IrH(CO)(dppe)_2^{2+}$ (VI) occurs (Scheme IV). The compound formed initially is the deprotonation product $Ir(CO)(dppe)_2^+$, and the reaction continues slowly to give VI. Hydroxide ion irreversibly deprotonates complex V. Again, attack at carbon monoxide does not occur. Thus V is unusually acidic for a third-row transition-metal complex.

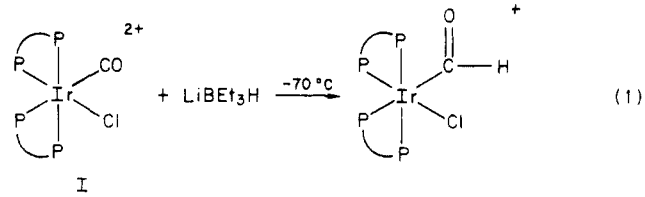
(iv) *trans*-IrH(CO)(dppe)$_2^{2+}$. The complex *trans*-$IrH(CO)(dppe)_2^{2+}$ (VI), like *trans*-$IrCl(CO)(dppe)_2^{2+}$ (III), shows no reactivity with water. Unlike III, however, VI loses CO on refluxing in an acetone/water solution to give an orange solution that contains $IrH(dppe)_2^{2+}$ and $Ir(dppe)_2^+$ (Scheme V). However, if VI is refluxed for 7 h in acetone/water with a CO purge through the solution, no reaction occurs.

Complex VI reacts readily with OH^- at room temperature to form *trans*-$IrH(CO_2H)(dppe)_2^+$ (VII) and the deprotonation product $Ir(CO)(dppe)_2^+$. Addition of acid to a solution of VII reforms VI (Scheme V), a reaction analogous to that of *trans*-$IrCl(CO_2Me)(dppe)_2^+$ (II) with acid to yield *trans*-$IrCl(CO)(dppe)_2^{2+}$ (IIIa) (Scheme I).

Reaction of the Complexes *cis*- and *trans*-IrX(CO)(dppe)$_2^{2+}$ (X = H, Cl) with Hydride Donating Agents. An initial attempt to prepare a formyl complex involved the reaction of $LiBEt_3H$ with *cis*-$[IrCl(CO)(dppe)_2][BF_4]_2$ (I) at low temperature. A reaction, which was monitored by NMR spectroscopy, occurs at −70 °C in CD_2Cl_2 to give a new compound that we formulate as *cis*-$IrCl(CHO)(dppe)_2^+$ (eq 1). The ^1H NMR spectrum

Scheme V



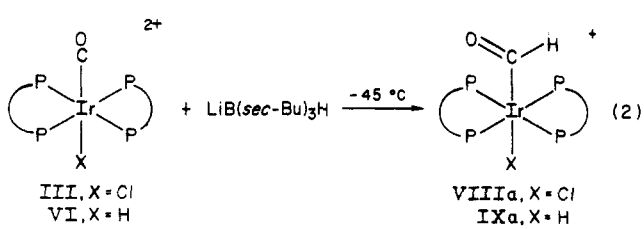


(1)

of this compound shows a doublet of multiplets centered at 12.9 ppm ($J_{formyl-P(trans)}$ = 58 Hz) for the formyl proton. A similar multiplet was observed by Thorn for *cis*-$IrH(CHO)(PMe_3)_4^+$ (δ_{CHO} 14.0 ($J_{formyl-P(trans)}$ = 49 Hz)).[19] Also appearing in the ^1H NMR spectrum of *cis*-$IrCl(CHO)(dppe)_2^+$ is a multiplet centered at 6.5 ppm, upfield of the main phenyl resonances, indicative of a cis geometry. The $^{31}P\{^1H\}$ NMR spectrum is very complex with broad lines and is temperature dependent. A detailed investigation of the presumed fluxional process was not undertaken. However it may involve phosphine dissociation since at −40 °C a resonance arising from *trans*-$IrCl(CHO)(dppe)_2^+$ (VIIIa) (vide infra) appears.

Isolation of *cis*-$IrCl(CHO)(dppe)_2^+$ has not been achieved. Reaction of $LiBEt_3H$ and I in CH_2Cl_2 at −78 °C followed by addition of ether results in the precipitation of an off-white solid. Low-temperature filtration gives a solid that rapidly decomposes on warming to room temperature. The solid also decomposes on standing at −50 °C.

The complexes *trans*-$[IrX(CHO)(dppe)_2][BF_4]$ (X = Cl (VIIIa), H (IXa)) are prepared by the addition of $LiB(sec\text{-}Bu)_3H$ to *trans*-$[IrX(CO)(dppe)_2][BF_4]_2$ in CH_2Cl_2 at −45 °C (eq 2). Complexes VIII and IX are stable in the

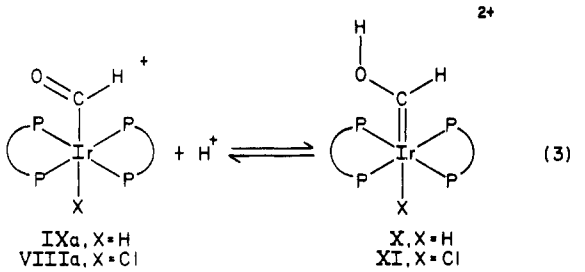


(2)

solid state, although IX turns orange under laboratory lighting. Both formyl complexes decompose readily at

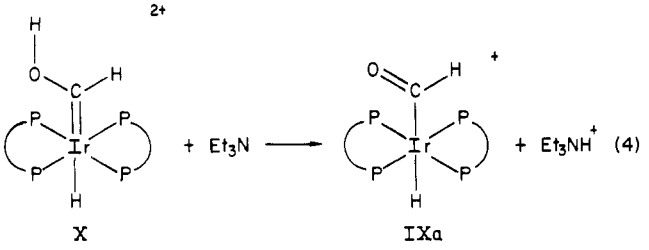
room temperature in halogenated solvents to form $IrHCl(dppe)_2^+$. In acetone, however, IXa shows only minimal decomposition to $Ir(CO)(dppe)_2^+$ after 6 h at room temperature.

Reaction of the Complexes *trans*-[IrX(CHO)(dppe)$_2$][BF$_4$] (X = Cl, H) with Acid. $HBF_4 \cdot Et_2O$ reacts instantaneously with the complexes *trans*-[IrX(CHO)(dppe)$_2$][BF$_4$] (X = H (IXa), Cl (VIIIa)) at −50 °C to yield the hydroxycarbene complexes *trans*-[IrX(CHOH)(dppe)$_2$][BF$_4$]$_2$ (X = H (X), Cl (XI)) (eq 3). ^1H NMR



(3)

spectra of a sample of X, prepared in situ at −50 °C in $CDCl_3$, clearly show the proton resonances of the hydride, hydroxyl, and carbene groups. Spectra of the isolated material at the same temperature in $CDCl_3$ show a single broad low-field resonance and a slightly shifted hydride resonance. (The $^{31}P\{^1H\}$ NMR spectra are identical.) This hydride resonance sharpens to a quintet of doublets when the sample is warmed to room temperature. An exchange process involving reversible O-protonation may be taking place. This is consistent with the fact that X is deprotonated readily by Et_3N to afford the formyl complex IXa (eq 4). Proton transfer is much more facile for complex



(4)

XI, the chloro derivative, than for X. Although the complex *trans*-[IrCl(CHO)(dppe)$_2$][BF$_4$], VIIIa, reacts readily with $HBF_4 \cdot Et_2O$ to afford a complex whose spectra are consistent with *trans*-$IrCl(CHOH)(dppe)_2^{2+}$ (XI) by analogy with X, this product cannot be isolated and decomposes in solution upon warming to form *cis*-$IrH(CO)(dppe)_2^{2+}$.

Elemental analysis of an isolated sample of X indicates the presence of a diethyl ether molecule. ^1H NMR spectra (Figure 1) of this material suggest that ether is bound to X, rather than simply cocrystallized, since the methylene (4.5 ppm) and methyl (1.2 ppm) resonances are shifted from those of free diethyl ether (3.3 and 1.1 ppm, respectively). With time these resonances slowly decrease in intensity and are replaced by those of free diethyl ether. Addition of ether to the sample results in the reappearance of the 4.5 and 1.2 ppm resonances. These results suggest that this dicationic carbene complex is highly electrophilic and reversibly binds diethyl ether at the carbene carbon atom.

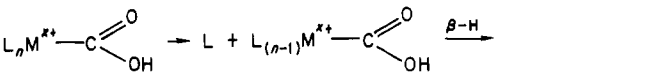
Discussion

Reactivity of IrX(CO)(dppe)$_2^{2+}$ with H_2O and OH^-. In this study we have examined the reactivity of a series of dicationic carbonyl complexes, $IrX(CO)(dppe)_2^{2+}$ (X = H, Cl), with water and hydroxide ion. These complexes show varied reactivity with water. The CO ligand of *cis*-$IrCl(CO)(dppe)_2^{2+}$ (I) is very electrophilic, reacting with water at −15 °C to afford $IrHCl(dppe)_2^+$ and CO_2. The trans isomers *trans*-$IrCl(CO)(dppe)_2^{2+}$ (III) and *trans*-$IrH(CO)(dppe)_2^{2+}$ (VI), however, are surprisingly stable and do not react at elevated temperatures. The complex *cis*-$IrH(CO)(dppe)_2^{2+}$ (V) is structurally similar to I and has a similar C≡O stretching frequency; yet the initial reaction of V with water involves deprotonation to form $Ir(CO)(dppe)_2^+$.

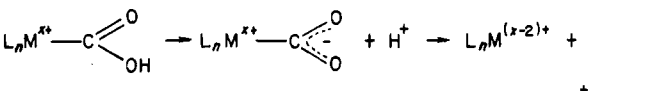
We have previously discussed the interaction of *cis*-$IrH(CO)(dppe)_2^{2+}$ (V) with H_2O, OH^-, and other bases.[33] The chemistry of V is dominated by its Brönsted acidity, being readily deprotonated by strong (NaOH, LiB(*sec*-Bu)$_3$H) and by weak (H_2O, Et_3N, pyridine) bases. Through initial interaction with the hydride ligand, chloride ion and water isomerize V to the trans isomer. Thus, the most electrophilic site in *cis*-$IrH(CO)(dppe)_2^{2+}$ is not the CO ligand but rather the "hydride" ligand. While first-row transition-metal hydrides can be very acidic, the more basic third-row transition-metal complexes typically are not. Deprotonation can be achieved in certain cases with strong bases, such as alkoxide.[37]

The reaction of coordinated carbon monoxide with water or hydroxide has often been presumed to proceed through an intermediate hydroxycarbonyl complex.[2,8] Few of these complexes have actually been isolated, however. Characterized examples include $IrCl_2(CO_2H)(CO)(PMe_2Ph)_2$,[36a] $(\eta\text{-}C_5H_5)Fe(CO_2H)(CO)(PPh_3)$,[38] $(\eta\text{-}C_5H_5)Re(CO_2H)(NO)(L)$ (L = CO,[28] PPh_3,[24a]), and $Pt(CO_2H)Cl(PEt_3)_2$.[39] The direct observation of the complex *trans*-$IrH(CO_2H)(dppe)_2^+$ (VII) and the isolation of *trans*-$IrCl(CO_2Me)(dppe)_2^+$ (II) in this study suggest that hydroxycarbonyl intermediates are also involved in the reactions of water or hydroxide ion with *cis*- and *trans*-$IrCl(CO)(dppe)_2^{2+}$. An understanding of the modes of decomposition of these intermediates leads to a possible explanation for the relative stability of VII.

Two decomposition routes have been suggested for hydroxycarbonyl complexes.[2,8a] The decomposition product could be either a reduced metal complex or a metal hydride. One route involves β-hydrogen elimination to form directly a metal–hydrogen bond. This process requires a vacant coordination site on the metal (eq 5). Alternatively, reductive decarboxylation can occur by initial deprotonation to form an intermediate carbon dioxide complex and subsequent dissociation of CO_2 with reduction of the transition-metal center (eq 6). (In eq 5 and 6, x refers to the oxidation state of the metal.)



(5)



(6)

The complexes *cis*- and *trans*-$IrCl(CO)(dppe)_2^{2+}$ immediately react with OH^- at low temperature to afford

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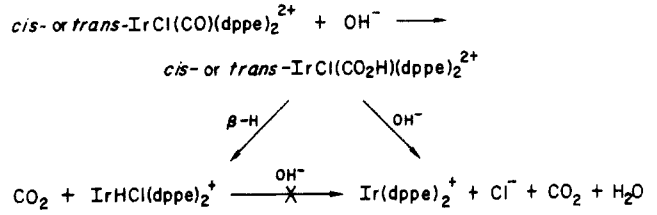
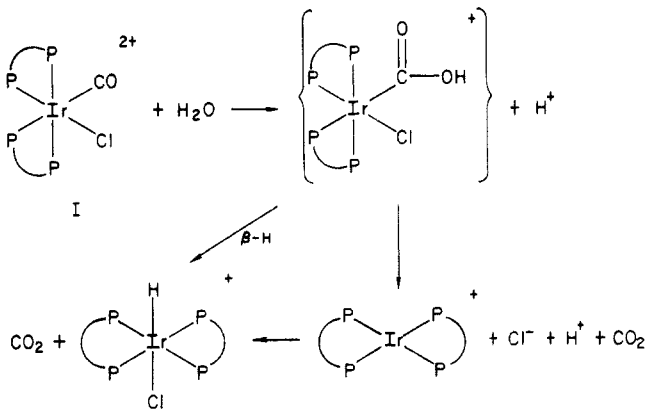
Scheme VI



Scheme VII

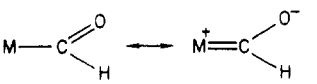


$Ir(dppe)_2^+$. Scheme VI outlines two possible pathways in the formation of this product. Although β-hydrogen elimination of an intermediate hydroxycarbonyl complex would directly yield $IrHCl(dppe)_2^+$ which, upon reaction with hydroxide ion, could form $Ir(dppe)_2^+$, this process can be ruled out since reaction of $IrHCl(dppe)_2^+$ with OH^- does not take place under the conditions of the experiment. In the second pathway deprotonation of the hydroxycarbonyl ligand with a second equivalent of hydroxide ion, followed by CO_2 loss, forms $Ir(dppe)_2^+$. This route of reductive decarboxylation to an intermediate CO_2 complex is the one that occurs for these complexes in basic media. The presumed intermediate *trans*-$IrCl(CO_2)(dppe)_2$ is analogous to the carbon dioxide complexes $MCl(CO_2)(LL)_2$ (M = Rh, Ir; LL = $Et_2PCH_2CH_2PEt_2$, $Me_2PCH_2CH_2PMe_2$) reported by Herskovitz and co-workers.[40] Stability of these CO_2 adducts was found to increase with increasing transition-metal basicity and with decreasing bulk of the chelating ligand. CO_2 dissociation should be facile from *trans*-$IrCl(CO_2)(dppe)_2$ owing to the lower basicity and greater bulk of dppe compared with $Me_2PCH_2CH_2PMe_2$.

Under acidic conditions the presumed intermediate *cis*-$IrCl(CO_2H)(dppe)_2^+$, formed from the reaction of water with *cis*-$IrCl(CO)(dppe)_2^{2+}$, decomposes to $IrHCl(dppe)_2^+$. $IrHCl(dppe)_2^+$ may be formed by either of the two modes presented in Scheme VII. The β-hydrogen elimination route requires a vacant coordination site. A strong intramolecular interaction between phenyl groups and the cis, nonphosphine ligands is observable by ^1H NMR spectroscopy for *cis*-$IrCl(CO)(dppe)_2^{2+}$ [33] and is typically seen for similar complexes in the cis geometry.[41] The increased bulk of the hydroxycarbonyl ligand in *cis*-$IrCl(CO_2H)(dppe)_2^+$ intensifies this interaction and facilitates phosphine dissociation. By analogy, note that only *trans*-$IrCl(CO_2Me)(dppe)_2^+$ is formed in the reaction of *cis*-$IrCl(CO)(dppe)_2^{2+}$ with $MeOH/Et_3N$, although the cis methoxycarbonyl complex must initially be formed since *cis*-$IrCl(CO)(dppe)_2^{2+}$ is stereochemically rigid. We believe that the bulk of the methoxycarbonyl ligand promotes phosphine dissociation and that this dissociation is the preliminary step in the isomerization to form the less sterically hindered isomer.

The second possible mode of decomposition of *cis*-$IrCl(CO_2H)(dppe)_2^+$ is reductive decarboxylation. Initial deprotonation would form an iridium–CO_2 complex that again should readily lose CO_2 for both steric and electronic reasons. The $Ir(dppe)_2^+$ thus formed would react with liberated H^+ in the presence of Cl^- to form the observed product $IrHCl(dppe)_2^+$.

The complex *trans*-$[IrH(CO_2H)(dppe)_2][BF_4]$ (VII), formed by the reaction of hydroxide ion with *trans*-$[IrH(CO)(dppe)_2][BF_4]_2$, is relatively stable in solution. However, the analogous complex *trans*-$[IrCl(CO_2H)(dppe)_2][BF_4]$ is not stable, as it decomposes in basic solution via reductive decarboxylation. Since the differences in coordination geometry between these two hydroxycarbonyl complexes should be minimal, the reason for the stability of VII is probably an electronic one. The electron density trans to the hydride ligand is greater than that trans to the chloride ligand in these complexes. This is expected since hydride is a stronger trans labilizing ligand than chloride.[42] That hydride is a stronger electron donor than chloride is clearly reflected in the formyl C=O stretching frequencies (Table I) for *trans*-$IrCl(CHO)(dppe)_2^+$ (VIIIa, 1625 cm^{-1}) and *trans*-$IrH(CHO)(dppe)_2^+$ (IXa, 1590 cm^{-1}). This implies a greater contribution from B for IXa; i.e., more electron density resides on a ligand



A B

trans to hydride than on one trans to chloride. Hence the $-CO_2H$ group in VII is more electron rich and therefore less acidic than in *trans*-$IrCl(CO_2H)(dppe)_2^+$, making reductive decarboxylation less likely. In addition decomposition of *trans*-$IrH(CO_2H)(dppe)_2^+$ by β-hydrogen elimination is hindered by the coordinative saturation of this complex.

Reactivity of $IrX(CO)(dppe)_2^{2+}$ with Hydride Donating Agents. Transition-metal formyl complexes have been of recent interest as models for intermediates thought to be present in carbon monoxide hydrogenation catalysis. Since the first preparation of a stable formyl complex, $Fe(CHO)(CO)_4^-$, by Collman and Winter in 1973,[14] a great deal of effort has been spent preparing and studying the reactivity of these complexes.[15] Synthetic routes to formyl complexes include the reaction of CO with certain transition-metal hydride complexes,[16,17] reactions with formylating agents, such as acetic formic anhydride,[14] direct oxidative addition of formaldehyde,[18,19] and nucleophilic attack of hydride on coordinated CO.[20-22] Of these methods, the first three are successful only with the most reactive systems and are therefore limited in scope. Hydride addition, however, is relatively straightforward and generally applicable. Thus trialkyl- and trialkoxyborohydride reagents have been used extensively to prepare a large number of anionic and neutral formyl complexes, many of which are thermally unstable.[15,43,44] Cationic

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formyl complexes are scarce. Only two types, IrH(CHO)$(PMe_3)_4^+$[19] and M(CHO)(CO)$(dppe)_2^+$ (M = Ru, Os),[23] have appeared in the literature.

Each of the compounds *cis*- and *trans*-IrX(CO)$(dppe)_2^{2+}$ (X = H, Cl) reacts with trialkylborohydrides. We have prepared two new cationic formyl complexes, *trans*-IrH(CHO)$(dppe)_2^+$ (IXa) and *trans*-IrCl(CHO)$(dppe)_2^+$ (VIIIa) by the reaction of LiB(*sec*-Bu)$_3$H with the corresponding trans hydrido and chloro carbonyl dications. A transient formyl complex formulated as *cis*-IrCl(CHO)$(dppe)_2^+$ forms when $LiBEt_3H$ is added to a solution of *cis*-IrCl(CO)$(dppe)_2^{2+}$. The instability of this complex may be related to the increased steric bulk of the formyl relative to the CO ligand. As mentioned above, bulky ligands in the cis position could lead to phosphine dissociation. Coordinatively unsaturated formyls are unstable with respect to hydride migration to the metal center.[20a] The low-temperature reaction of *cis*-IrH(CO)$(dppe)_2^{2+}$ (V) with LiB(*sec*-Bu)$_3$H, as expected on the basis of the Brönsted acidity of V, affords the deprotonation product Ir(CO)$(dppe)_2^+$. H_2 is presumably liberated.

Hydroxycarbene species have been suggested to be important intermediates in carbon monoxide hydrogenation processes.[12] A rare example of O-protonation of a formyl ligand to afford a hydroxycarbene complex[24] is the reaction of *trans*-IrH(CHO)$(dppe)_2^+$ (IXa) or *trans*-IrCl(CHO)$(dppe)_2^+$ (VIIIa) with HBF_4. Although protonation occurs at the formyl oxygen atom in both cases, as shown by NMR spectroscopy, only *trans*-[IrH(CHOH)$(dppe)_2$][BF_4]$_2$ (X) is isolable owing to the greater basicity of the formyl oxygen atom in IXa, illustrative of the greater contribution of resonance form B for IXa compared with VIIIa. Proton exchange is apparently facile in both complexes since a resonance for the hydroxyl proton could not be observed in ^{1}H NMR spectra of isolated X and *trans*-IrCl(CHOH)$(dppe)_2^{2+}$ prepared in situ. Similarly, the hydroxyl protons could not be observed in ^{1}H NMR spectra of the related methyl hydroxycarbene complexes (η-C_5H_5)Fe(C(OH)Me)(CO)$(PPh_3)^+$,[45] MnX(C(OH)Me)$(CO)_4$ (X = Br, I),[46] and ReX(C(OH)Me)$(CO)_4$ (X = Cl, Br, I).[47] An exchange process is also suggested by a broadening of the hydride resonance of X as the temperature is lowered. The acidity of the hydroxyl proton in this complex is confirmed by the reaction with NEt_3, in which *trans*-IrH(CHO)$(dppe)_2^+$ (IXa) is regenerated.

The complexes *trans*-[IrH(CHOH)$(dppe)_2$][BF_4]$_2$ and [(η-C_5H_5)Re(CHOH)(NO)(PPh_3)]X (X = SO_3CF_3, *p*-$CH_3C_6H_4SO_3$)[24] are the only known examples of isolated and characterized hydroxycarbene complexes. Stable salts of (η-C_5H_5)Re(CHOH)$(PPh_3)(NO)^+$ have been prepared by Gladysz and co-workers by the reaction of (η-C_5H_5)Re(CHO)(PPh_3)(NO) with the strong acids HSO_3CF_3 and *p*-$CH_3C_6H_4SO_3H$.[24] The weaker acid CF_3CO_2H at −70 °C also gives the hydroxycarbene complex. However this salt is unstable above −40 °C where it decomposes to a mixture of (η-C_5H_5)Re(CO)$(PPh_3)(NO)^+$ and (η-C_5H_5)Re(Me)(PPh_3)(NO). These workers suggest that the protonation reaction is reversible and that a disproportionation takes place that involves hydride transfer from trace amounts of the formyl to the electrophilic carbon atom of the hydroxycarbene ligand. Similar schemes involving hydroxycarbene intermediates have been proposed for the acid-induced decomposition reactions of anionic and neutral formyl complexes.[25,26,48]

The carbene carbon atom of *trans*-IrH(CHOH)$(dppe)_2^{2+}$ is highly electrophilic and reversibly binds diethyl ether as evidenced by ^{1}H NMR spectroscopy and elemental analysis. In spite of this electrophilicity and the presence of equilibrium amounts of *trans*-IrH(CHO)$(dppe)_2^+$ hydride transfer does not occur. This may reflect a lower degree of hydridic character for the formyl hydrogen atom as expected for these cationic formyl complexes. On the other hand, a bimolecular interaction, as presumably occurs in the above cited cases, may be unfavorable owing to the steric bulk of the dppe ligands. These electronic and steric factors no doubt contribute to the stability of *trans*-[IrH(CHOH)$(dppe)_2$][BF_4]$_2$ (X). This complex is much more stable than the related formyl complex *trans*-[IrH(CHO)$(dppe)_2$][BF_4] (IXa). We do not know the details of the decomposition of IXa. However formyl complexes often decompose by hydride migration to the metal center[20a] or by hydride transfer processes.[21] Protonation of the O atom to form the hydroxycarbene complex suppresses these processes and may be viewed as Lewis acid stabilization of the formyl complex.[49]

In halogenated solvents *trans*-IrH(CHO)$(dppe)_2^+$ (IXa) decomposes to IrHCl$(dppe)_2^+$. The complex *trans*-[IrCl(CHO)$(dppe)_2$][BF_4] (VIIIa) also decomposes to give the same product. This similarity in decomposition together with the observation that IXa is relatively stable in non-halogenated solvents suggests to us that IXa decomposes by initial chlorine atom extraction to form *trans*-IrCl(CHO)$(dppe)_2^+$. Further decomposition presumably involves either phosphine or chloride dissociation followed by hydride migration to the iridium center. Displacement of CO by the dissociated ligand forms the observed product.

Chloride dissociation may be favored over phosphine dissociation in VIIIa owing to the strong trans influence of the formyl ligand. Metal–chlorine and metal–hydrogen stretching frequencies in octahedral Ir(III) complexes have been used as a measure of the trans influence of the trans ligand.[42] Lower stretching frequencies indicate a larger trans influence. The Ir–Cl stretching frequency for VIIIa (Table I) is very low, 220 cm^{-1}, and is in the range typical for chlorine trans to acyl. For complexes of the type IrCl(L)$(dppe)_2^{n+}$ in this study, decreasing trans influence based on Ir–Cl stretching frequencies follows the order CHO (220 cm^{-1}) > H (255 cm^{-1}) > CO_2Me (270 cm^{-1}) > P (300 cm^{-1}; complex I, L = CO) > CO (310 cm^{-1}). The strong trans influence of the formyl ligand is also evident from the low Ir–H stretching frequency, 1940 cm^{-1}, observed for IXa. Decreasing trans influence, based on Ir–H stretching frequencies for complexes of the type IrH(L)$(dppe)_2^{n+}$, follows the order CHO (1940 cm^{-1}) > CHOH (2040 cm^{-1}) > CO_2H (2080 cm^{-1}) > P (2140 cm^{-1}; complex V, L = CO) > CO(2160 cm^{-1}) > Cl (2220 cm^{-1}). Both sets of data give a consistent ordering of the relative trans influencing strengths of these ligands. Of the ligands containing carbon and oxygen, formyl is by far the strongest trans influencing ligand and is closely related to acyl.

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Conclusions

The stabilities of the formyl and hydroxycarbonyl complexes prepared in this study are related to their coordinative saturation and to the steric and electronic conditions at the iridium center. Thus complexes of cis geometry, in which there is a strong steric interaction, tend to be unstable. For example, *cis*-$IrCl(CHO)(dppe)_2^+$ is not stable above −50 °C and *cis*-$IrCl(CO_2H)(dppe)_2^+$, the presumed intermediate in the reaction of *cis*-$IrCl(CO_2H)(dppe)_2^{2+}$ with H_2O and OH^-, is not observable at all. The trans isomers of these formyl and hydroxycarbonyl complexes are more stable and, except for *trans*-$IrCl(CO_2H)(dppe)_2^+$, can be isolated and characterized. An electronic effect, the increased electron density trans to the hydride ligand, seems to be the major reason for the stability of *trans*-$IrH(CO_2H)(dppe)_2^+$. This effect also explains the stability of *trans*-$IrH(CHOH)(dppe)_2^{2+}$ relative to *trans*-$IrCl(CHOH)(dppe)_2^{2+}$. The complex *trans*-$IrH(CHOH)(dppe)_2^{2+}$ is in turn more stable in solution than the formyl complex $IrH(CHO)(dppe)^{2+}$. This increased stabilization in the presence of a Lewis acid is probably a result of suppression of the usual modes of decomposition that formyl complexes exhibit, i.e., hydride migration to the metal and hydride transfer reactions, and suggests that hydroxycarbene complexes could be very important intermediates in the reduction of carbon monoxide.

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Registry No. I, 91606-11-0; II, 94570-04-4; IIIa, 91685-25-5; IIIb, 94596-64-2; IV, 66673-10-7; V, 91685-23-3; VI, 66350-34-3; VII, 94570-06-6; VIIIa, 94570-08-8; VIIIb, 94570-15-7; IXa, 94570-10-2; IXb, 94570-17-9; X, 94570-12-4; *trans*-$[IrCl(CO)(dppe)_2]Cl_2$, 94570-13-5; $Ir(CO)(dppe)_2^+$, 40264-88-8; *cis*-$IrH_2(dppe)_2^+$, 47898-62-4; $LiB(sec\text{-}Bu)_3H$, 38721-52-7; $LiBEt_3D$, 74540-86-6; $Ir(dppe)_2^+$, 29871-99-6; $IrH(dppe)_2^{2+}$, 66350-22-9; CO, 630-08-0; $[IrH(CHOH)(OEt_2)(dppe)_2][BF_4]_2$, 94570-19-1; $LiBEt_3H$, 22560-16-3.

Communications

New Bimetallic Cobalt(II) Complexes of Chelated, Bridged Phosphido Ligands

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Summary: Treatment of cobaltocene with secondary phosphines (e.g., R_2PH or the linked bis(secondary diphosphines) $H(Ph)P(CH_2)_nP(Ph)H$, n = 2, 3) produces phosphido-bridged dicobalt complexes **1–5** that contain a Co–Co bond. Reactions of **1–5** with SO_2 at ambient conditions lead to insertion of SO_2 into the Co–Co bond, whereas $HBF_4 \cdot OEt_2$ produces dicobalt cations in which the bridging hydrogen atom bonding can be represented as a closed two-electron, three-center interaction.

Our research group has recently shown that tertiary–secondary diphosphine ligands of the type $R_2PCH_2CH_2CH_2P(H)Ph$ provide rational and controlled routes to phosphido-bridged bimetallic complexes.[1] Syntheses of phosphido and arsenido-bridged compounds have become an active field of research based on the reasonable assumption that these compounds would possess strong binding properties and help maintain the integrity of $M–PR_2–M$ bridges in bimetallic complexes and small metal clusters.[2] However our results,[2d] as well as several other recent reports,[2a,3–5] indicate that $M–PR_2–M$ bridges are more reactive than previously thought. We have attempted to improve the stability of the bridging phosphido linkage by incorporating it into the chain of a chelating ligand.[1] Flood[6a] reported the first example of a linked (i.e., via a trimethylene chain) phosphido bridge; two other reports have appeared recently, in which bridging phosphido ligands are connected by *o*-phenylene[6b] and *o*-xylene[6c] linkages in iron carbonyl complexes. Herein, we report the syntheses, ^{31}P NMR data, and the structures of dicobalt complexes of linked bridging bis(phosphido) ligands.

Hayter,[7] Werner,[8] Dahl,[9] and their co-workers have prepared and studied the binuclear complexes $[(C_5R_5)M-$

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