over the two possible rotamers. Following isotropic refinement and pairwise constrained refinement of the sulfur and C12 populations, an absorption correction was applied using the DIFABS absorption correction program. Full least-squares anisotropic refinement (except for sulfur, which was isotropic) of the structure with hydrogens placed in idealized positions based upon a difference Fourier map converged with R_1 = 0.0363 and R_2 = 0.0399.

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Registry No. 1, 81971-46-2; **2**, 131323-30-3; **3**, 136953-53-2; Cp*Rh(PMe$_3$)H$_2$, 84624-03-3; Cp*Rh(PMe$_3$)(2-C$_4$H$_3$S)Br, 136953-54-3; Cp*Rh(PMe$_3$)Br$_2$, 88704-26-1; Cp*Rh(PMe$_3$)(2-C$_4$H$_3$S)$_2$, 136953-55-4; Cp*Rh(PMe$_3$)(2-C$_4$H$_3$)(Cl), 136953-56-5; Cp*Rh(PMe$_3$)Cl$_2$, 80298-79-9; Cp*Rh(PMe$_3$)(2-C$_4$H$_3$S)(D), 136953-57-6; Cp*Rh(PMe$_3$)(2-C$_4$H$_2$S-4-Me)Cl, 137038-74-5; Cp*Rh(PMe$_3$)(2-C$_4$H$_2$S-4-Me)H, 136953-58-7; Cp*Rh(PMe$_3$)(SCH=CMeCH=CH), 136953-59-8; Cp*Rh(PMe$_3$)(SCH=CHCMe=CH), 136953-60-1; Cp*Rh(PMe$_3$)(2-C$_4$H$_2$-5-Me)Cl, 136953-61-2; Cp*Rh(PMe$_3$)(2-C$_4$H$_2$-5-Me)Br, 136953-62-3; Cp*Rh(PMe$_3$)(SCMe=CHCH=CH), 131323-32-5; Cp*Rh(PMe$_3$)(3-C$_4$H$_3$S)Br, 136953-63-4; Cp*Rh(PMe$_3$)(3-C$_4$H$_3$S)H, 136953-64-5; Cp*Rh(PMe$_3$)(2-C$_4$H$_2$DS)H, 136953-65-6; 2-ThLi, 2786-07-4; C$_4$Me$_4$S, 14503-51-6; thiophene, 110-02-1; 3-methylthiophene, 616-44-4; 2-methylthiophene, 554-14-3; 3-bromothiophene, 872-31-1; 3,4-bis(chloromethyl)-2,5-dimethylthiophene, 5368-70-7; 2,5-dimethylthiophene, 638-02-8.

Supplementary Material Available: Tables S-I–S-VI of bond distances and angles, coordinates of atoms, and anisotropic thermal parameters (7 pages); listing of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

Calorimetric Studies of the Heats of Protonation of the Metal in Fe(CO)$_3$(bidentate phosphine, arsine) Complexes: Effects of Chelate Ligands on Metal Basicity

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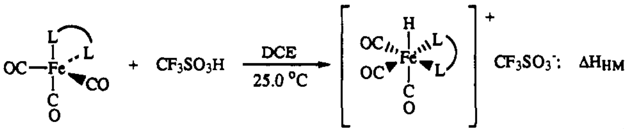
Abstract: Titration calorimetry has been used to determine the heats of protonation (ΔH_{HM}) of Fe(CO)$_3$(L⌒L) complexes (L⌒L = dppm, dppe, dppp, dppb, dppbz, *cis*-dppv, arphos, dmpm, dcpe, and diars) with CF$_3$SO$_3$H in 1,2-dichloroethane solution at 25.0 °C. Spectroscopic studies show that protonation occurs at the metal center to form *fac*-[Fe(H)(CO)$_3$(L⌒L)]CF$_3$SO$_3$. For the series Fe(CO)$_3$[Ph$_2$P(CH$_2$)$_n$PPh$_2$], n = 1–4, ΔH_{HM} becomes less exothermic as the chelate size increases from n = 1 (−24.0 ± 0.2 kcal mol^{-1}) to n = 4 (−20.1 ± 0.2 kcal mol^{-1}). Moreover, the chelate complexes are substantially more basic than the related nonchelate complex Fe(CO)$_3$(PPh$_2$Me)$_2$ (ΔH_{HM} = −17.6 ± 0.4 kcal mol^{-1}). Likewise, Fe(CO)$_3$(dmpm) is much more basic (ΔH_{HM} = −30.2 ± 0.4 kcal mol^{-1}) than Fe(CO)$_3$(PMe$_3$)$_2$ (ΔH_{HM} = −23.3 ± 0.3 kcal mol^{-1}). The higher basicities of complexes with small chelate ligands are ascribed to distortions imposed on the Fe(CO)$_3$(L⌒L) complexes by the chelate ligand. Basicities of several other Fe(CO)$_3$(L⌒L) complexes are also discussed.

Introduction

Bidentate phosphines and arsines are commonly used chelating ligands in transition-metal complex chemistry.[1] The effects of the chelates on the properties and reactivities of metal complexes have been the subject of several investigations.[2] However, little is known of the effects of bidentate phosphine and arsine ligands on the basicities of such complexes.[3]

In this paper, we examine how chelate size and basicity controls the basicities of Fe(CO)$_3$(L⌒L) complexes, as measured by their heats of protonation (ΔH_{HM}) with CF$_3$SO$_3$H in 1,2-dichloroethane (DCE) solvent at 25.0 °C (eq 1). Comparisons are made with ΔH_{HM} values of analogous monodentate phosphine complexes Fe(CO)$_3$(L)$_2$. In previous calorimetric studies of basicities were reported the heats of protonation of monophosphines (PR$_3$),[4a] diphosphines,[4b] and a series of methylcyclopentadienyl complexes



(1)

where L⌒L is

Ph$_2$P(CH$_2$)PPh$_2$ (dppm)
Ph$_2$P(CH$_2$)$_2$PPh$_2$ (dppe)
Ph$_2$P(CH$_2$)$_3$PPh$_2$ (dppp)
Ph$_2$P(CH$_2$)$_4$PPh$_2$ (dppb)
Ph$_2$P(1,2-C$_6$H$_4$)PPh$_2$ (dppbz)
cis-Ph$_2$P(CH=CH)PPh$_2$ (cis-dppv)
Ph$_2$P(CH$_2$)$_2$AsPh$_2$ (arphos)
Me$_2$P(CH$_2$)PMe$_2$ (dmpm)
Cy$_2$P(CH$_2$)$_2$PCy$_2$ (dcpe)
Me$_2$As(1,2-C$_6$H$_4$)AsMe$_2$ (diars)

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Cp'Ir(1,5-COD) (Cp' = $C_5Me_xH_{5-x}$, x = 0, 1, 3-5), in which protonation occurs at the Ir.[5]

Experimental Section

All preparative reactions and manipulations were carried out under an atmosphere of nitrogen using Schlenk techniques similar to those described by McNally et al.[6] Hexanes and CH_2Cl_2 were refluxed over CaH_2 and then distilled.[7] Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Deuteriochloroform was stored over molecular sieves in air or distilled from P_2O_5 under nitrogen. The phosphine and arsine ligands were purchased from commercial sources.

The ^{1}H NMR spectra were recorded in $CDCl_3$ (except as stated otherwise) on a Nicolet-NT 300 MHz spectrometer using TMS (δ = 0.00 ppm) as the internal reference. The $^{31}P\{^1H\}$ NMR spectra were recorded in 10-mm tubes on a Bruker WM 200 NMR spectrometer in $CDCl_3$ using 85% H_3PO_4 (δ = 0.00 ppm) as the external standard. A Digilab FTS-7 FT-IR spectrophotometer was used for recording solution infrared spectra. Mass spectra were obtained on a Finnigan 4000 instrument, and the elemental microanalysis of $\mathbf{1}H^+CF_3SO_3^-$ was performed by Galbraith Laboratories Inc., Knoxville, TN.

Synthesis of Fe(CO)$_3$($L^\frown L$). Although complexes **1**,[8] **2**,[8a,9] **3**,[10] **5**,[11] **6**,[12] and **10**[9e,f,13] have been prepared previously by other methods, all of the complexes in this study were synthesized from reactions of Fe(CO)$_3$(bda)[14a] (bda = benzylideneacetone) with the appropriate phosphine. The purity and characterization of each compound were established by infrared and ^{1}H NMR spectroscopies.

Samples for ^{1}H and $^{31}P\{H\}$ NMR spectra were prepared by dissolving ~10 mg of each compound in 0.5 mL of $CDCl_3$ under N_2. The solutions were filtered under a nitrogen flow through a short plug of Celite (~2 × 0.5 cm) directly into an NMR tube to remove paramagnetic impurities. An additional 0.5 mL of $CDCl_3$ for ^{1}H NMR samples and 2 mL for $^{31}P\{H\}$ NMR samples was then passed through the column to elute any remaining compound.

Fe(CO)$_3$(dppbz) (5). A solution of Fe(CO)$_3$(bda)[14a] (0.49 g, 1.7 mmol) in THF (35 mL) was treated with a slight excess of 1,2-bis(diphenylphosphino)benzene (0.85 g, 1.9 mmol). The mixture was stirred for 24 h at room temperature. At this time the IR spectrum showed three new bands (ν(CO) (cm^{-1}) THF 1986 s, 1916 m (sh), 1903 s) for **5** and no bands corresponding to the starting material. The mixture was filtered, and the solvent was removed under vacuum. The oily residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on a column of neutral alumina (15 × 3 cm, ~150 mesh) with a 1:3 mixture of CH_2Cl_2/hexanes. The first yellow-orange band was collected, and the solvent was evaporated under vacuum. Recrystallization by dissolving the residue in a minimum amount of CH_2Cl_2, layering with a 10-fold volume of hexanes, and then cooling to −20 °C for ~24 h afforded orange crystals of **5** (0.63 g, 64%): ^{1}H NMR δ 7.40–7.56 (m, C_6H_5, C_6H_4); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1985 s, 1913 m (sh), 1897 s.

Data for Compounds 1–4 and 6–10. Below are given yields, reaction times, and spectral data for the other Fe(CO)$_3$($L^\frown L$) complexes prepared by the above method.

Fe(CO)$_3$(dppm) (1): reaction time, 16 h; yield, 81%; MS (70 eV) *m/e* 524 (M$^+$), 496 (M$^+$ − CO), 468 (M$^+$ − 2CO), 440 (M$^+$ − 3CO); ^{1}H NMR δ 4.22 (t, 2 H, $^2J_{PH}$ = 10.8 Hz, CH_2), 7.37 (m, Ph), 7.55 (m, Ph); $^{31}P\{H\}$ NMR δ 14.87 (s); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1984 s, 1911 m (sh), 1901 s.

Fe(CO)$_3$(dppe) (2): reaction time, 16 h; yield, 52%; MS (70 eV) *m/e* 538 (M$^+$), 510 (M$^+$ − CO), 482 (M$^+$ − 2CO), 454 (M$^+$ − 3CO); ^{1}H NMR[9a] δ 2.44 (m, 4 H), 7.39–7.57 (m, Ph); $^{31}P\{H\}$ NMR[9a] δ 96.08 (s); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1982 s, 1913 m, 1892 s.

Fe(CO)$_3$(dppp) (3): reaction time, 16 h; yield, 52%; MS (70 eV)[10] *m/e* 552 (M$^+$), 524 (M$^+$ − CO), 496 (M$^+$ − 2CO), 468 (M$^+$ − 3CO); ^{1}H NMR δ 1.93 (m, 2 H, CH_2), 2.43 (pseudoquintet, $^2J_{HH}$ = $^2J_{PH}$ = 5.2 Hz, 4 H, P(CH_2)), 7.31 (m, Ph), 7.45 (m, Ph); $^{31}P\{H\}$ NMR[10] δ 46.35 (s); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1982 s, 1909 m, 1881 s.

Fe(CO)$_3$(dppb) (4): reaction time, 16 h; yield, 72%; MS (70 eV) *m/e* 566 (M$^+$), 538 (M$^+$ − CO), 510 (M$^+$ − 2CO), 482 (M$^+$ − 3CO); ^{1}H NMR δ 1.73 (br s, 4 H, CH_2), 2.40 (br s, 4 H, P(CH_2)), 7.35 (m, Ph), 7.49 (m, Ph); $^{31}P\{H\}$ NMR δ 57.12 (s); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1981 s, 1908 m, 1879 s.

Fe(CO)$_3$(*cis*-dppv) (6): reaction time, 26 h; yield, 67%; ^{1}H NMR[12] δ 7.38–7.50 (m, Ph), =CH not identified; IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1988 s, 1918 m (sh), 1897 s.

Fe(CO)$_3$(arphos) (7): reaction time, 16 h; yield, 55%; ^{1}H NMR δ 2.19 (dt, $^2J_{PH}$ = 23.9 Hz, $^2J_{HH}$ = 7.0 Hz, 2 H, P(CH_2)), 2.47 (q, $^2J_{HH}$ = $^2J_{PH}$ = 7.0 Hz, 2 H, As(CH_2)), 7.34–7.56 (m, Ph); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1982 s, 1910 m, 1890 s.

Fe(CO)$_3$(dmpm) (8): reaction time, 16 h; yield, 53%; ^{1}H NMR (CD_2Cl_2, decomposes in $CDCl_3$) δ 1.63 (t, $^2J_{PH}$ = 5.1 Hz, 12 H, CH_3), 3.23 (t, J_{PH} = 11.0 Hz, 2 H, CH_2); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1978 s, 1901 m (sh), 1884 s.

Fe(CO)$_3$(dcpe) (9): reaction time, 16 h; yield, 20%; ^{1}H NMR δ 1.24–1.93 (m, Cy and CH_2); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1968 s, 1890 s (sh), 1871 s.

Fe(CO)$_3$(diars) (10): reaction time, 20 h; yield, 38%; ^{1}H NMR (CD_2Cl_2, decomposes in $CDCl_3$)[13] δ 1.67 (s, 12 H, Me), 7.67 (m, 4 H, C_6H_4); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 1979 s, 1904 m (sh), 1885 s.

Protonation Reactions. Compounds **1–10** were protonated by dissolving approximately 30 mg of each compound in 3 mL of CH_2Cl_2 under N_2. To the solution was added 1 equiv of CF_3SO_3H by microliter syringe. Immediately the color of the solution was bleached from the yellow or orange color of the neutral complex to pale yellow or pale orange, respectively. The IR spectrum showed the complete disappearance of the bands corresponding to the starting material and appearance of new bands at higher frequency for the [Fe(H)(CO)$_3$($L^\frown L$)]$^+$ products. Solutions of the protonated complexes are fairly stable as long as they are kept under N_2, but when exposed to air they readily decompose. Upon adding 1 equiv of 1,3-diphenylguanidine base in CH_2Cl_2 solvent the original color immediately reappeared as did the IR bands corresponding to the unprotonated starting material. Samples for ^{1}H NMR spectra of **1H$^+$–10H$^+$** were prepared by adding 1 equiv of CF_3SO_3H to solutions of the neutral complexes in $CDCl_3$ which were prepared as described above.

Isolation of [Fe(H)(CO)$_3$(dppm)]CF$_3$SO$_3$ (1H$^+$CF$_3$SO$_3^-$). To a stirred solution of **1** (0.18 g, 0.34 mmol) in CH_2Cl_2 (4.0 mL) was added 1 equiv of CF_3SO_3H. The solution was then layered with Et_2O (15 mL) and cooled slowly to −78 °C. It was stored at that temperature for 3 days giving pale yellow air-sensitive crystals of **1**H$^+$CF$_3$SO$_3^-$ (0.18 g, 79%): ^{1}H NMR δ 4.31 (dt, $^2J_{H_bH_c}$ = 16.8 Hz, $^2J_{PH_c}$ = 13.2 Hz, 1 H, H_c), 5.57 (m, 9 lines, $^2J_{PH_b}$ = 10.5 Hz,[15] 1 H, H_b), 7.59 (m, Ph), 7.80 (m, Ph), −6.53 (td, $^2J_{PH}$ = 42.6 Hz, $^4J_{H_aH_b}$ = 3.9 Hz, 1 H, Fe-H, H_a); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2090 s, 2039 s. Anal. Calcd for $C_{29}H_{23}F_3FeO_6P_2S$: C, 51.65; H, 3.44. Found: C, 51.44; H, 3.85.

[Fe(H)(CO)$_3$(dppe)]CF$_3$SO$_3$ (2H$^+$CF$_3$SO$_3^-$): ^{1}H NMR δ 2.68 (m, 2 H, CH_2), 3.46 (m, 2 H, CH_2), 7.5–8.0 (m, Ph), −8.97 (t, $^2J_{PH}$ = 43.9 Hz, 1 H, Fe-H); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2094 s, 2042 s.

[Fe(H)(CO)$_3$(dppp)]CF$_3$SO$_3$ (3H$^+$CF$_3$SO$_3^-$): ^{1}H NMR δ 1.83 (br m, 2 H, CH_2), 2.95 (br m, 4 H, CH_2), 7.45 (m, Ph), 7.65 (m, Ph), −7.49 (t, $^2J_{PH}$ = 40.4 Hz, 1 H, Fe-H); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2087 s, 2034 s.

[Fe(H)(CO)$_3$(dppb)]CF$_3$SO$_3$ (4H$^+$CF$_3$SO$_3^-$): ^{1}H NMR δ 1.80 (br s, 4 H, CH_2), 2.80 (br s, 4 H, CH_2), 7.9 (m, Ph), −7.55 (t, $^2J_{PH}$ = 45.4 Hz, 1 H, Fe-H); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2091 s, 2033 s.

[Fe(H)(CO)$_3$(dppbz)]CF$_3$SO$_3$ (5H$^+$CF$_3$SO$_3^-$): ^{1}H NMR δ 7.4–8.0 (m, Ph), −8.76 (t, $^2J_{PH}$ = 44.3 Hz, 1 H, Fe-H); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2096 s, 2045 s.

[Fe(H)(CO)$_3$(*cis*-dppv)]CF$_3$SO$_3$ (6H$^+$CF$_3$SO$_3^-$): ^{1}H NMR δ 7.39–7.69 (m, Ph), =CH not identified, −9.50 (t, $^2J_{PH}$ = 45.5 Hz, 1 H, Fe-H); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2095 s, 2044 s.

[Fe(H)(CO)$_3$(arphos)]CF$_3$SO$_3$ (7H$^+$CF$_3$SO$_3^-$): ^{1}H NMR δ 2.25 (m, 1 H, CH_2), 2.75 (br m, 1 H, CH_2), 3.5 (m, 2 H, CH_2), 7.4–8.0 (m, Ph),

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−9.28 (d, $^2J_{PH}$ = 44.4 Hz, 1 H, Fe-H); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2089 s, 2038 s.

[Fe(H)(CO)$_3$(dmpm)]CF$_3$SO$_3$ (8H$^+$CF$_3$SO$_3$$^-$): ^{1}H NMR ($CD_2Cl_2$) δ 1.95 (t, J_{PH} = 6.5 Hz, 12 H, CH_3), 3.59 (m, 9 lines, $^2J_{PH_b}$ = 10.0 Hz,[15] 1 H, H_b), 3.82 (q, $^2J_{H_bH_c} = {}^2J_{PH_c}$ = 14.5 Hz, H_c), −7.75 (td, $^2J_{PH}$ = 45.6 Hz, $^4J_{HH}$ = 4.3 Hz, 1 H, Fe-H, H_a); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2087 s, 2031 s.

[Fe(H)(CO)$_3$(dcpe)]CF$_3$SO$_3$ (9H$^+$CF$_3$SO$_3$$^-$): ^{1}H NMR δ 1.25–1.95 (br m, Cy and CH_2), −9.95 (t, $^2J_{PH}$ = 43.8 Hz, 1 H, Fe-H); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2079 s, 2023 s.

[Fe(H)(CO)$_3$(diars)]CF$_3$SO$_3$ (10H$^+$CF$_3$SO$_3$$^-$): ^{1}H NMR ($CD_2Cl_2$) δ 2.00 (s, 6 H, CH_3), 2.07 (s, 6 H, CH_3), 7.8–8.0 (m, 4 H, Ph), −10.64 (s, 1 H, Fe-H); IR (CH_2Cl_2) ν(CO) (cm^{-1}) 2089 s, 2034 s.

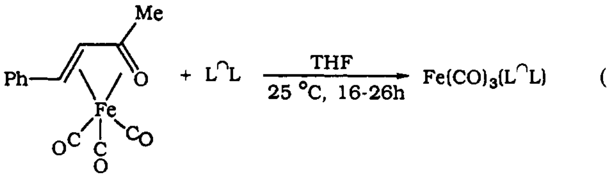
Calorimetry Studies

Determinations of the heats of protonation of the Fe(CO)$_3$(L⌒L) compounds were performed using a Tronac Model 458 isoperibol calorimeter as previously described.[4,5] Typically a run consisted of three sections:[16] initial heat capacity calibration, titration (at 25.0 °C), and final heat capacity calibration. Each section was preceded by a baseline acquisition period. The titration period involved the addition of 1.2 mL of a 0.1 M CF_3SO_3H solution (standardized to a precision of ±0.0002 M) in 1,2-dichloroethane (DCE) at a constant rate during 3 min time to 50 mL of a 2.6 mM solution of Fe(CO)$_3$(L⌒L) (10% excess) in DCE. The Fe(CO)$_3$(L⌒L) solutions were prepared by adding the solid compound to an argon-filled Dewar flask. The flask was then attached to the calorimeter's insert assembly, flushed with argon, and 50 mL of DCE was added by syringe. The reaction enthalpies were corrected for the heat of dilution (ΔH_{dil})[5] of the acid in DCE (−0.2 kcal mol^{-1}).

To ensure reproducibility of the determined ΔH_{HM} values, at least two different standardized acid solutions were used for the titrations of each compound. The ΔH_{HM} values are reported as the average of at least four titrations, and as many as six, for each compound. The error is reported as the average deviation from the mean of all the determinations.

Results

Synthesis of Fe(CO)$_3$(L⌒L). Complexes **1–10** in this study are prepared from Fe(CO)$_3$(bda)[14a] (bda = benzylideneacetone) in yields ranging from 20% for **9** to 81% for **1** (eq 2). This method is of general use for the synthesis of Fe(CO)$_3$(L⌒L) complexes.[17,18]



(2)

Complexes **1–10** should be stored under N_2 (or vacuum); **8–10** are especially air-sensitive and can be handled only for brief periods in air. Solutions of **1–10** are stable as long as they are kept under N_2 or Ar.

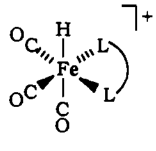
The observation of three ν(CO) bands in the solution infrared spectra (CH_2Cl_2) of **1–10** is consistent with these complexes having approximately trigonal-bipyramidal structures[19] with phosphine ligand donors coordinated in axial and equatorial sites. The structures of **1**,[8b] **2**,[9c] **5**,[11] and **10**[13] determined by X-ray crystallography have been described as having distorted trigonal-bipyramidal or square-pyramidal geometries.

Singlet resonances in the ^{31}P{H} NMR spectra of **1–4** and **5**[11] at room temperature indicate that the PPh_2 groups in these molecules are equivalent. This is probably due to the fluxionality[10] of the Fe(CO)$_3$(L⌒L) molecules (L⌒L = bidentate phosphine), which has been studied in detail previously[10] and is probably accomplished by relatively minor movements of the CO and L groups.[8b,9c,10] As observed in other phosphine chelate complexes,[20] the ^{31}P{H} NMR chemical shifts in Fe(CO)$_3$(L⌒L) depend on the size of the L⌒L chelate ring.

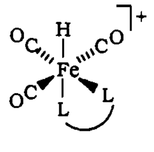
Protonation Reactions of Fe(CO)$_3$(L⌒L). Bidentate complexes **1–10** were protonated with 1 equiv of CF_3SO_3H in CH_2Cl_2 solution as shown in eq 1. Only the protonation of **10** has been described previously and then only as a personal communication to the authors in ref 21. These reactions occur immediately as indicated by the bleaching of the solution color, the disappearance of the starting complex ν(CO) bands, and the appearance of new ν(CO) bands at higher frequencies than those of the corresponding neutral starting complexes. These shifts in the ν(CO) bands are characteristic of protonation at the metal.[22]

Solutions of **1H$^+$–10H$^+$** are stable as long as they are kept under a nitrogen or argon atmosphere. Complex **1H$^+$**CF$_3$SO$_3$$^-$ was isolated (79% yield) and fully characterized; however, the solid compound decomposes immediately upon exposure to air. No attempts were made to isolate the analogous complexes **2H$^+$–10H$^+$**; they were characterized by their IR and NMR spectra.

The two possible geometries for the protonated products are the fac (**A**) and mer (**B**) isomers. Infrared spectra of **1H$^+$–10H$^+$** show two strong bands in the ν(CO) region; the symmetric band at higher frequency (2096–2079 cm^{-1}) is sharp, but that at lower frequency (2045–2023 cm^{-1}) is broad. Ideally a fac geometry would be expected to give three strong bands[23] as is found for the analogous *fac*-M(H)(CO)$_3$(dppe) (M = Mn, Re) complexes.[24] On the other hand, *fac*-Re(H)(CO)$_3$(dppm)[24b] has only two bands, but the lower frequency absorption in CH_2Cl_2 solvent (1927 cm^{-1}) is reported to be about twice as broad as that at higher frequency (2011 cm^{-1}). The Raman spectrum of the Re dppm complex, however, shows three separate lines at 2002, 1921, and 1908 cm^{-1}. Thus, the broad IR band at 1927 cm^{-1} of Re(H)(CO)$_3$(dppm) consists of two unresolved absorptions. There are also only two bands in the IR spectrum of Mn(H)(CO)$_3$(dppm)[25] when taken in CH_2Cl_2 (2000, 1917 cm^{-1}), but three bands are found in *n*-hexane indicating poorer resolution in the more polar CH_2Cl_2 solution.[19] It is thus reasonable to consider that the broad band at lower frequency for **1H$^+$–10H$^+$** consists of two unresolved absorptions which would be consistent with the fac (**A**) geometry for these protonated complexes. The mer isomer B is much less likely since the equivalent trans CO groups would be expected to give a weak ν(CO) absorption at high frequency for the symmetric stretching mode.



A



B

The ^{1}H NMR spectra of **1H$^+$–10H$^+$** show one resonance in the high field region typical of metal hydrides,[21,27] which indicates

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(15) Coupling constant was determined by spectrum simulation using a curve fitting method supplied by New Methods for Research, Inc., Syracuse, NY.

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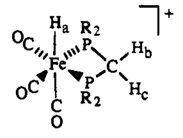
Table I. Heats of Protonation (ΔH_{HM}) of $Fe(CO)_3(L\frown L)$ and $Fe(CO)_3(L)_2$ Complexes and the Uncoordinated Phosphines[a]

$Fe(CO)_3(L\frown L)$,[b] $Fe(CO)_3(L)_2$	$-\Delta H_{HM}$, kcal mol^{-1}	chelate ring size	$-\Delta H_{HP1}$,[c] kcal mol^{-1}	$-\Delta H_{HP2}$,[d] kcal mol^{-1}
$Fe(CO)_3$(dppm), **1**	24.0 (±0.2)[e]	4	22.0 (±0.1)	14.9 (±0.2)
$Fe(CO)_3$(dppe), **2**	23.2 (±0.1)	5	22.8 (±0.2)	20.2 (±0.1)
$Fe(CO)_3$(dppp), **3**	21.1 (±0.2)	6	23.4 (±0.1)	22.4 (±0.3)
$Fe(CO)_3$(dppb), **4**	20.1 (±0.2)	7	24.6 (±0.1)	23.8 (±0.2)
$Fe(CO)_3$(dppbz), **5**	23.4 (±0.2)	5	21.3 (±0.1)	10.7 (±0.3)
$Fe(CO)_3$(*cis*-dppv), **6**	23.1 (±0.3)	5	19.9 (±0.3)	10.0 (±0.2)
$Fe(CO)_3$(arphos), **7**	22.6 (±0.1)	5	23.2 (±0.4)	8.2 (±0.1)
$Fe(CO)_3$(dmpm), **8**	30.2 (±0.4)	4	31.0 (±0.3)	25.8 (±0.2)
$Fe(CO)_3$(dcpe), **9**	28.4 (±0.2)	5		
$Fe(CO)_3$(diars), **10**	26.5 (±0.3)	5		
$Fe(CO)_3(PPh_2Me)_2$	17.6 (±0.4)[f]		24.7 (±0.0)[g]	
$Fe(CO)_3(PMe_3)_2$	23.3 (±0.3)[f]		31.6 (±0.2)[g]	

[a] For protonation with CF_3SO_3H (0.1 M) in DCE solvent at 25.0 °C. [b] Ligand abbreviations: $Ph_2P(CH_2)PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp), $Ph_2P(CH_2)_4PPh_2$ (dppb), $Ph_2P(1,2\text{-}C_6H_4)PPh$ (dppbz), *cis*-$Ph_2P(CH{=}CH)PPh_2$ (*cis*-dppv), $Ph_2P(CH_2)_2AsPh_2$ (arphos), $Me_2P(CH_2)PMe_2$ (dmpm), $Cy_2P(CH_2)_2PCy_2$ (dcpe); $Me_2As(1,2\text{-}C_6H_4)AsMe_2$ (diars). [c] Represents the addition of 1 equiv of CF_3SO_3H to 1 equiv of the free phosphine; see ref 4b. [d] Represents the addition of second equiv of CF_3SO_3H to 1 equiv of the free phosphine; see ref 4b. [e] Numbers in parentheses are average deviations. [f] Reference 31. [g] ΔH_{HP}, ref 4a.

that only one isomer is present. The occurrence of this resonance as a triplet, due to coupling to the equivalent phosphorus atoms in the bidentate phosphine complexes **1**H^+, **6**H^+, **8**H^+, and **9**H^+, supports the assignment of the fac (**A**) geometry for these complexes. For complexes **1**H^+ and **8**H^+ each triplet is further split into a doublet. Selective decoupling experiments were performed to identify the source of the extra coupling. Irradiation of the CH_2 multiplet resonance of the dppm ligand at 5.57 ppm for **1**H^+ reduced the Fe–H triplet of doublets resonance at −6.53 ppm to a triplet. Similarly for **8**H^+, irradiation of the CH_2 multiplet of dmpm at 3.59 ppm resulted in a triplet for the Fe–H resonance at −7.75. Thus, the fine structure of these hydride resonances results from long-range coupling with one of the methylene protons of the dppm ($^4J_{HH}$ = 3.9 Hz) or dmpm ($^4J_{HH}$ = 4.3 Hz) ligand (see structure **C**). The complexes Re(H)(CO)$_3$(dppm)[24b] and (C_5Me_5)Ru(H)(dppm)[3c] have also been reported to exhibit a similar type of long-range coupling ($^4J_{HH}$ = 4.0 and 3.5 Hz, respectively). It is likely that the coupling is between protons H_a and H_b in structure **C** because of the "w-conformation" found between the two nuclei.[28]



C

Previously, it was noted for *fac*-Mn(CH$_3$)(CO)$_3$(dppm)[26] that the observed chemical shift inequivalence of the methylene protons in the dppm ligand (H_b and H_c) indicated a static geometry at the Mn atom. The inequivalence of the methylene protons in **1**H^+ and **8**H^+ show that these complexes are also stereochemically nonfluxional in contrast to the neutral complexes.

The hydride resonance for the arphos complex **7**H^+ occurs as a doublet at −9.28 ppm, $^2J_{PH}$ = 44.4 Hz. Because the $^2J_{PH}$ value is similar to those for the other bidentate phosphine complexes, **7**H^+ presumably also has the fac geometry. Complex **10**H^+ has only a singlet hydride resonance (−10.64 ppm) because the diars ligand contains no phosphorus atoms. The Me groups on the ligand in **10**H^+ are split into two singlets, 2.00 and 2.07 ppm, from the two Me groups cis to the hydride ligand and two trans to Fe–H.

Calorimetric Studies. Heats of protonation (ΔH_{HM})[29] of the bidentate complexes **1**–**10** determined by calorimetric titration are presented in Table I. The values range from −20.1 kcal mol^{-1} for complex **4** to −30.2 kcal mol^{-1} for **8**. As expected for titrations of reactions which occur stoichiometrically, rapidly, and without significant decomposition of the reactant or product, titration plots of temperature vs amount of acid added are linear.[16] Titrations of the air-sensitive complexes **8**, **9**, and **10** exhibited a slight amount of decomposition as evidenced by increased slopes during the pre- and posttitration baseline segments. However, the increase in baseline slope is only ~5% of the titration slope indicating that the heat contributed by decomposition is relatively small and the effect on the ΔH_{HM} values is probably within the experimental error.

Because DCE has a low dielectric constant (ϵ = 10.36) the products formed in eq 1 probably occur as ion pairs. Dissociation of these ion pairs, and autoprotolysis and dimerization of the acid are other reactions which may occur in nonpolar solvents such as DCE. An analysis of these factors was presented previously in studies of the heats of protonation of phosphines;[4a] it was concluded that they contribute less than 2% to the total ΔH_{HP} value. Presumably these reactions also contribute negligibly to ΔH_{HM} values in the current study.

A factor which could potentially affect the ΔH values obtained in this and our other protonation studies in DCE is the ion-pairing energy of the products. Protonated products $HB^+CF_3SO_3^-$ with small HB^+ cations would be expected to have higher ion-pairing energies than those with large HB^+ cations. There are several lines of evidence that indicate such energies do not vary greatly with the size of the cation. First, the solvent appears to have little effect on the relative basicities of simple phosphines PR_3 since there is an excellent correlation[4a,b] between ΔH_{HP} values for phosphine protonation in DCE with their pK_a's in water. Second, the phosphonium ions $HPPh_3^+$ and $HPCy_3^+$ of approximately the same size have vastly different ΔH_{HP} values, −21.2 and −33.2 kcal mol^{-1}, respectively; also the much smaller $HPMe_3^+$ has a less exothermic ΔH_{HP} value (−31.6 kcal mol^{-1}) than $HPCy_3^+$ (−33.2 kcal mol^{-1}). Furthermore, [Fe(H)(CO)$_3$(dppe)]CF_3SO_3 (**2**$H^+CF_3SO_3^-$) and [Fe(H)(CO)$_3$(dcpe)]CF_3SO_3 (**9**$H^+CF_3SO_3^-$) which have cations of similar size have quite different ΔH_{HM} values, −23.2 and −28.4 kcal mol^{-1}, respectively. Thus, it is unlikely that ion-pairing energies dominate the trends in basicities observed in this or our other heat of protonation studies in DCE.

Also listed in Table I are the heats of protonation, ΔH_{HP1} and ΔH_{HP2}, for the free bidentate ligands[4b,30] under the same conditions (25.0 °C, in DCE solution) with 1 and 2 equiv of CF_3SO_3H. The ΔH_{HP1} and ΔH_{HP2} values correspond predominantly to the reactions in eqs 3 and 4 for ligands (e.g., dppm and dppe) where there is a substantial difference between ΔH_{HP1} and ΔH_{HP2}. When this difference is small as for dppb, both reactions 3 and 4 occur simultaneously, as discussed previously,[4b] and have essentially the same values of ΔH_{HP1} and ΔH_{HP2}.

$$P\frown P + CF_3SO_3H \xrightarrow[25.0\ °C]{DCE} HP\frown P^+CF_3SO_3^- \quad (3)$$

$$HP\frown P^+CF_3SO_3^- + CF_3SO_3H \xrightarrow[25.0\ °C]{DCE} HP\frown PH^{2+}(CF_3SO_3^-)_2 \quad (4)$$

Discussion

Dependence of ΔH_{HM} on Chelate Size in Fe(CO)$_3$[Ph$_2$P(CH$_2$)$_n$PPh$_2$]. We have determined ΔH_{HM} for a series of Fe-

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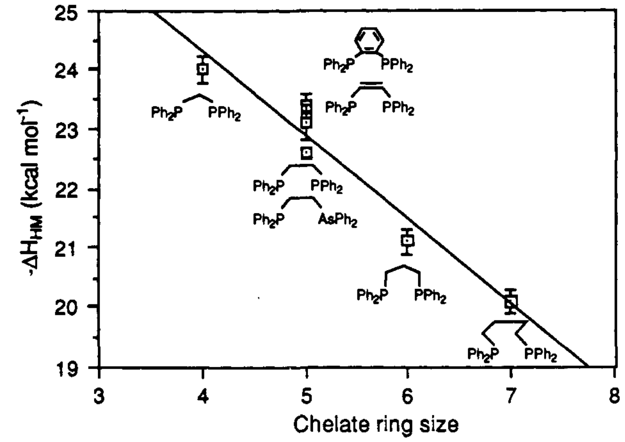
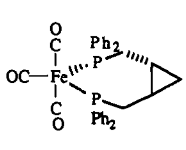


Figure 1. Effect of chelate ring size on the basicity (ΔH_{HM}) of the iron center in the $Fe(CO)_3(L\frown L)$ complexes.

$(CO)_3[Ph_2P(CH_2)_nPPh_2]$, **1**–**4**, complexes where *n* in the bidentate ligand backbone varies from 1 to 4; the structures of reactants and products as established by spectroscopic and in a few cases X-ray diffraction studies are shown in eq 1. As seen from the data in Table I, the basicity of the metal in these complexes is greatest (ΔH_{HM} = −24.0 kcal mol^{-1}) for the smallest chelate (*n* = 1) and smallest (ΔH_{HM} = −20.1 kcal mol^{-1}) for *n* = 4. In terms of equilibrium constants *K* for protonation, assuming $\Delta S°$ is the same for both reactions as is nearly true for protonations of other neutral complexes,[5] $Fe(CO)_3$(dppm) (**1**) is 723 times more basic than $Fe(CO)_3$(dppb) (**4**). A plot (Figure 1) of ΔH_{HM} vs the chelate ring size in **1**–**4** shows the trend of decreasing basicity of the complex with increasing chelate ring size.

In attempting to explain this trend, one might consider differences in the donor abilities of the $Ph_2P(CH_2)_nPPh_2$ ligands that might lead to differences in the basicities of their complexes. In a study[31] of monodentate phosphine complexes $Fe(CO)_3(PR_3)_2$, we have shown that increasing the basicity of the phosphine increases the basicity of the complex. In the present situation, however, increasing the basicity of the $Ph_2P(CH_2)_nPPh_2$[4b,30] from −22.0 kcal mol^{-1} (ΔH_{HP}, Table I) for *n* = 1 (dppm) to −24.6 kcal mol^{-1} for *n* = 4 (dppb) *decreases* the basicity of the complex. Since ligand basicity does not explain the effect of chelate ring size on complex basicity, we suggest that it is the distortion of the complex imposed by the chelate which most affects the basicity of the $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ complexes. The structure adopted and predicted by theoretical calculations[32] for all $Fe(CO)_3(PR_3)_2$ complexes containing monodentate phosphines has both phosphines in the axial positions of a trigonal-bipyramid (eq 5). Since this is the most stable geometry, any distortion imposed on it by a bidentate ligand would make it less stable; this higher energy geometry apparently is also more basic. From X-ray diffraction studies reported in the literature, it is evident that the structures of $Fe(CO)_3(P\frown P)$ complexes change substantially depending on the chelate ring size. Thus, the P–Fe–P angle in **1**[8b] (chelate ring size = 4) is only 73.5° as compared with 84.1° in the dppe complex (**2**)[9c] (chelate ring size = 5). For $Fe(CO)_3$[*trans*-1,2-bis((diphenylphosphino)methyl)cyclopropane] (**D**),[17] which has the same chelate ring size (7) as **4**, the P–Fe–P angle is 123.9°. Increasing the chelate ring size to 8 in $Fe(CO)_3$[2,2′-bis((diphenylphosphino)methyl)-1,1′-biphenyl] (**E**)[17] increases the P–Fe–P angle to 152.0°. Thus, increasing the chelate ring size from 4 to 8 causes a dramatic increase in the P–Fe–P angle from 73.5° to 152.0°. This increase in the P–Fe–P angle is accompanied by a decrease in the basicity of the complex. This trend suggests that the diaxial complex $Fe(CO)_3(PPh_2Me)_2$ will be less basic than any of the



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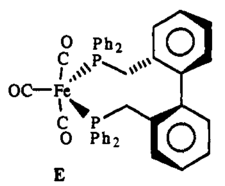
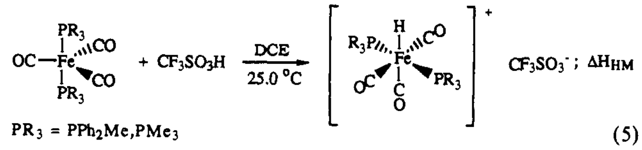


E

$Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ complexes. This is indeed true as ΔH_{HM} for this complex (Table I) is only −17.6 kcal mol^{-1}.[31] This value for $Fe(CO)_3(PPh_2Me)_2$ compares with −20.1 kcal mol^{-1} for **4**, which has the largest chelating ligand. (It should be noted that both the PPh_2Me and dppb ligands have about the same basicity, ΔH_{HP} = −24.7 kcal mol^{-1} (Table I).) If the complex is distorted even further as with the smaller dppm ligand, the complex becomes even more basic.

Extended Hückel MO calculations[32] for d^8 ML_5 systems indicate that on going from trigonal-bipyramidal (TBP) to square-pyramidal (SQP) geometry along a Berry pseudorotation coordinate, the energy of the HOMO rises; presumably it is this orbital that is protonated in the complexes in the current study. The $Fe(CO)_3(PPh_2Me)_2$ and $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$, *n* = 1–4, complexes appear to undergo such a transformation in geometry as the chelate size decreases; this is evident in the TBP geometry of $Fe(CO)_3(PPh_2Me)_2$ and the approximate SQP geometry of $Fe(CO)_3$(dppm) **1**.[8b,9c] Although this transformation occurs over a lower symmetry coordinate than is described by a Berry pseudorotation,[17] the analogy supports the interpretation that structural differences in the geometry of the reactants control the metal basicity.

These interpretations of the data in Table I are based on structural differences in the $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ and $Fe(CO)_3(PPh_2Me)_2$ reactants. However, it is possible that there are differences in energy in the protonated products especially since the $\{Fe(H)(CO)_3[Ph_2P(CH_2)_nPPh_2]\}^+$ (eq 1) complexes have a fac geometry and $[Fe(H)(CO)_3(PPh_2Me)_2]^+$ has a mer structure (eq 5).[31] The mer structure is presumably more stable than the fac since $[Fe(H)(CO)_3(PPh_2Me)_2]^+$ with the unconstraining monodentate ligands adopts this geometry. The fac geometry of



(5)

the chelate complexes $\{Fe(H)(CO)_3[Ph_2P(CH_2)_nPPh_2]\}^+$ would then be of higher energy. Thus, if the relative basicities (ΔH_{HM}) of the $Fe(CO)_3(PPh_2Me)_2$ and $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ complexes were determined by the energies of the protonated products, $Fe(CO)_3(PPh_2Me)_2$ would be more basic than the chelated complexes. Since this is not the case, it appears that it is distortion by the chelate ligands of the reactants which makes the $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ complexes more basic than $Fe(CO)_3(PPh_2Me)_2$. This conclusion is supported by a thermochemical study[2h] of the $Mo(CO)_4[Ph_2P(CH_2)_nPPh_2]$ (*n* = 1–4) complexes in which it was found that the *n* = 1 complex is ~6 kcal mol^{-1} higher in energy than *cis*-$Mo(CO)_4(PMePh_2)_2$; this destabilization was attributed to ring strain in the chelate complex.

The large chelate effects on metal complex basicity in the present system are illustrated by the equilibrium in eq 6. The difference between ΔH_{HM} values for $Fe(CO)_3(PPh_2Me)_2$ and **1**

$$Fe(H)(CO)_3(PPh_2Me)_2^+ + \underset{\mathbf{1}}{Fe(CO)_3(dppm)} \rightleftharpoons Fe(CO)_3(PPh_2Me)_2 + \underset{\mathbf{1H^+}}{Fe(H)(CO)_3(dppm)^+} \quad (6)$$

gives a value of −6.4 kcal mol^{-1} for the enthalpy of this reaction. Assuming $\Delta S°$ = 0 eu, as is nearly true for protonations of other related neutral complexes,[5] the equilibrium constant for eq 6 is 4.9×10^4. A very similar enhancement (−6.9 kcal mol^{-1}) in metal basicity is seen in the comparison of ΔH_{HM} values (Table I) for the chelate complex $Fe(CO)_3$(dmpm) (**8**) (−30.2 kcal mol^{-1}) and

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its monodentate analogue $Fe(CO)_3(PMe_3)_2$ (−23.3 kcal mol^{-1}).[31]

Effects on ΔH_{HM} of Other Bidentate Ligands in $Fe(CO)_3(L⌒L)$. The free bidentate ligands[4b,30] in complexes **5**–**7** are somewhat weaker donor ligands than dppe, as measured by their ΔH_{HP} values (Table I).[4b] This results from the relatively electron-withdrawing bridging groups, 1,2-C_6H_4 in dppbz and *cis*-CH=CH in *cis*-dppv, and the poorer donor ability of the $AsPh_2$ group in arphos. Despite the weaker donating abilities of these ligands, complexes **5**–**7** have ΔH_{HM} values that are essentially the same as that (−23.2 kcal mol^{-1}) of $Fe(CO)_3$(dppe). It appears that it is the chelate ring size of 5 which is common to these complexes, and, among complexes with similar ligand ΔH_{HP} values, it is the chelate ring size which is the most important factor controlling the ΔH_{HM} values of the complexes (Figure 1). As discussed above, the chelate ring size affects the amount of distortion in the complex and therefore the basicity of the metal. That the dppe and dppbz ligands induce similar degrees of distortion is supported by X-ray structures of **2**[9c] and **5**[11] which have P–Fe–P angles of 84.1° and 85.8°, respectively.

In complexes where the basicity of the ligand is changed more dramatically, the ΔH_{HM} values of the $Fe(CO)_3(L⌒L)$ complexes do indeed change. Thus, $Fe(CO)_3$(dmpm) (**8**) is 6.2 kcal mol^{-1} more basic than $Fe(CO)_3$(dppm) (**1**); in terms of the equilibrium in eq 7, **8** is 3.5 × 10^4 times more basic than **1** (assuming $\Delta S°$ = 0 eu).

$$\underset{\mathbf{1H^+}}{[Fe(H)(CO)_3(dppm)]^+} + \underset{\mathbf{8}}{Fe(CO)_3(dmpm)} \rightleftharpoons \underset{\mathbf{1}}{Fe(CO)_3(dppm)} + \underset{\mathbf{8H^+}}{[Fe(H)(CO)_3(dmpm)]^+} \quad (7)$$

Similarly, the cyclohexyl groups in dcpe make $Fe(CO)_3$(dcpe) (**9**) 5.2 kcal mol^{-1} more basic than $Fe(CO)_3$(dppe) (**2**). Jia and Morris[3c] have recently observed a similar trend as pK_a values of $[CpRuH_2(L⌒L)]BF_4$ complexes (in parentheses) increase with increasing σ-donor ability of the chelate: L⌒L = $(p\text{-}CF_3C_6H_4)_2P(CH_2)_2P(p\text{-}CF_3C_6H_4)_2$ (4.8) < $Ph_2P(CH_2)_2PPh_2$ (7.3) < $(p\text{-}MeOC_6H_4)_2P(CH_2)_2P(p\text{-}MeOC_6H_4)$ (8.8) < $Me_2P(CH_2)_2PMe_2$ (9.8). The lower basicity (−26.5 kcal mol^{-1}) of $Fe(CO)_3$(diars) (**10**) as compared with $Fe(CO)_3$(dcpe) (−28.4 kcal mol^{-1}) is presumably due to the weaker donor ability of arsines as compared to that of phosphines.[4b,33]

Conclusion

The most important result of these studies is the observation that chelating ligands increase the basicity (ΔH_{HM}) of the metal in the $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ (n = 1–4) complexes by 3.5–6.4 kcal mol^{-1}, depending on the chelate size, as compared to the analogous monodentate complex $Fe(CO)_3(PPh_2Me)_2$. That these are substantial changes in basicity is illustrated by the result that the equilibrium constant for the protonation of $Fe(CO)_3$(dppm) is 4.9 × 10^4 larger than that for $Fe(CO)_3(PPh_2Me)_2$, assuming $\Delta S°$ = 0 eu. We propose that a chelate-imposed distortion of the complexes from the most stable diaxial geometry of $Fe(CO)_3(PPh_2Me)_2$ causes the metal in the chelate complexes to be more basic: the greater the distortion from this geometry the greater the basicity of the metal. These results suggest that structural effects of chelates in other metal complexes may have a significant influence on the basicity of the metal.

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Registry No. 1, 137120-73-1; **1**$H^+CF_3SO_3^-$, 137038-89-2; **2**, 38894-55-2; **2**$H^+CF_3SO_3^-$, 137038-91-6; **3**, 56700-29-9; **3**$H^+CF_3SO_3^-$, 137038-93-8; **4**, 137120-74-2; **4**$H^+CF_3SO_3^-$, 137038-95-0; **5**, 119654-85-2; **5**$H^+CF_3SO_3^-$, 137038-97-2; **6**, 105954-72-1; **6**$H^+CF_3SO_3^-$, 137038-99-4; **7**, 137038-85-8; **7**$H^+CF_3SO_3^-$, 137039-01-1; **8**, 137038-86-9; **8**$H^+CF_3SO_3^-$, 137039-03-3; **9**, 137038-87-0; **9**$H^+CF_3SO_3^-$, 137039-05-5; **10**, 56760-75-9; **10**$H^+CF_3SO_3^-$, 137039-07-7; $Fe(CO)_3$(bda), 38333-35-6.

Yields of Singlet Molecular Oxygen from Peroxyl Radical Termination

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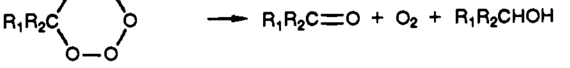
Abstract: The reaction, $2R_1R_2CHOO^\bullet \rightarrow R_1R_2CHOH + R_1R_2CO + O_2$ with R_1,R_2 = H or simple alkyl, gave 3–14% (mean = 8%) $^1O_2$ ($^1\Delta_g$) in *tert*-butylbenzene at 60–80 °C. The yields were lower in some peroxyls, with N or O atoms in the α- or β-positions of R_1 and R_2, and were small-to-negligible when the precursor could give a peroxyl which lacked α-H atoms (cumene, *t*-BuOOH, Me_2NCHO). Changes in temperature had little effect on the yield of $^1O_2$ in the title reaction, and yields changed about 10-fold in different solvents. Peroxyls derived from Ph_2CH_2 and Ph_2CD_2 gave identical (11–12%) yields of singlet oxygen relative to benzophenone. Since the yield of $^1O_2$ from the 9-fluorenylperoxyl self-reaction was only 6–10%, the intermediacy of triplet 9-fluorenone and $^3O_2$ could apparently be ruled out, because the latter gave 80–90% $^1O_2$ by photochemical approaches. A concerted decomposition of $(R_1R_2CHOO)_2$ by the "Russell" scheme to give $^1O_2$ ($^1\Sigma_g$), which then partitions between $^1\Delta_g$ and $^3\Sigma_g$, is in accord with most, but not all, of our experimental results.

Introduction

Peroxyl radicals react with each other by a *stepwise* (Vaughan[2] termination, eq 1, R = alkyl) process

$$2ROO^\bullet \rightleftharpoons ROO{-}OR \rightarrow RO^\bullet + O_2 + {}^\bullet OR \rightarrow ROOR \quad (1)$$

or in a faster process that is usually ascribed to a cyclic, *concerted* reaction (Russell[3] termination, eq 2) of the intermediate tetroxide:[4]



(2)

(R = H or alkyl)

The exothermicity of reaction 2 is sufficient to produce electronically excited states of either oxygen or carbonyl products. The formation of singlet oxygen was originally investigated by

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