$[(CH_3)_3NH][S_2P(CF_3)_2]$ (70°) produced a red solution from which traces of elemental sulfur sublimed (100° (10^{-4} Torr)), but no sublimable platinum complex was isolated. The mass spectrum (source temperature at 100°) of the red material showed an intense peak due to $PtS_4P_2(CF_3)_4$ and a barely detectable peak corresponding to $Pt_2S_6P_4(CF_3)_8$. The presence of peaks for the sulfur-deficient dimer is consistent with the formation of elemental sulfur. While K_2PtCl_4 is not soluble in dichloromethane, the product of the salt reaction is extractable into dichloromethane producing deep red solutions. The low volatility of this red material suggests the presence of a salt possibly analogous to $[(n\text{-}C_3H_7)_4N][Pd(S_2PF_2)_3]$.[22] Preliminary attempts to reduce Pt(IV) compounds with $(CF_3)_2P(S)SH$ have been unsuccessful. There seems to be no convincing reason why $Pt[S_2P(CF_3)_2]_2$ should not exist, and attempts to obtain it are continuing.

Acknowledgments.—We thank the National Research Council of Canada and the University of Alberta for financial support of this work. We wish to express our gratitude to Dr. B. Kratochvil for the polarographic results obtained in $Ni[S_2P(CH_3)_2]_2$ in acetonitrile. We are also indebted to Dr. A. R. Sanger for helpful discussions and some experimental assistance.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK AT BUFFALO,
BUFFALO, NEW YORK 14214

Infrared Intensities of the Carbonyl Stretching Vibrations in Cyclopentadienyliron Dicarbonyl Derivatives

BY DONALD J. DARENSBOURG

Received October 29, 1971

The integrated infrared intensities of the ν_{CO} stretching vibrations have been determined for a series of iron complexes of the types $(C_5H_5)Fe(CO)_2X$ (where X = Cl, I, CN, $SnCl_3$, or $C(O)CH_3$) and $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$ in chloroform solution. Dipole moment derivatives for the carbonyl stretching modes have been calculated assuming that the A′ and A″ vibrational modes each exhibit a characteristic MCO group moment derivative. Variations in these derivatives as a function of the angle (θ) between MCO groupings in the series of complexes have also been considered in detail. In all cases the dipole moment derivatives for the symmetric stretching motion were found to be substantially smaller than that of the corresponding derivatives for the asymmetric stretching motion. It is concluded on the basis of these results that the cyclopentadienyl ligand is primarily acting as a donor grouping in the complexes studied.

Introduction

The bonding in cyclopentadienyl(transition metal) carbonyls is a subject of active discussion by both theoretical and experimental chemists, and there are still several unanswered questions. The relative importance of the donor and acceptor bonding properties of the cyclopentadienyl ion is one of these unresolved issues. Semiempirical calculations on ferrocene have led to conflicting reports on the charge distribution in this molecule.[1-3] Recently, photoelectron spectroscopy measurements on several π-cyclopentadienylmetal complexes have indicated the ring carbons of the cyclopentadienyl residues to be slightly positively charged.[4] In order to aid in these discussions, as well as for their intrinsic value, the absolute infrared intensities of the carbonyl stretching vibrations in substituted cyclopentadienyliron carbonyl compounds have been measured in chloroform solution. Integrated intensity measurements of the infrared CO stretching vibrations in transition metal carbonyl compounds have given additional information on the electronic character of the CO groupings.[5-17] Specifically, the integrated infrared intensities of the CO stretching vibrations have been shown to be highly dependent on the extent of π bonding between the metal and CO.[11,14]

The compounds examined in this study were $(C_5H_5)Fe(CO)_2X$ (where X = Cl, I, CN, $SnCl_3$, or $C(O)CH_3$) and $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$. The experimental data were examined to find correlations between changes in the infrared intensities of the two CO stretching modes in these compounds and the nature of the affixed ligands $C_5H_5^-$ and X.

Experimental Section

Preparation of Compounds.—Cyclopentadienyliron dicarbonyl dimer (mp 194° dec) was obtained from Strem Chemicals, Inc. All reactions were performed under a dry nitrogen atmosphere. $(C_5H_5)Fe(CO)_2Cl$,[18] $(C_5H_5)Fe(CO)_2I$,[19] $(C_5H_5)Fe$-

---

[1] E. M. Shustorovish and M. E. Dyatkina, *Zh. Strukt. Khim.*, **1**, 109 (1960).

[2] J. P. Dahl and C. J. Ballhausen, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **33**, No. 5 (1961).

[3] I. H. Hillier and R. M. Canadine, *Discuss. Faraday Soc.*, **47**, 27 (1969).

[4] D. T. Clark and D. B. Adams, *Chem. Commun.*, 740 (1971).

[5] W. Beck and R. E. Nitzschmann, *Z. Naturforsch. B*, **17**, 577 (1962).

[6] K. Noack, *Helv. Chim. Acta*, **45**, 1847 (1962).

[7] R. D. Fischer, *Spectrochim. Acta*, **19**, 842 (1963).

[8] W. Beck, A. Melnikoff, and R. Stahl, *Angew. Chem., Int. Ed. Engl.*, **4**, 692 (1965).

[9] W. Beck, A. Melnikoff, and R. Stahl, *Chem. Ber.*, **99**, 3721 (1966).

[10] R. M. Wing and D. C. Crocker, *Inorg. Chem.*, **6**, 289 (1967).

[11] T. L. Brown and D. J. Darensbourg, *ibid.*, **6**, 971 (1967).

[12] E. W. Abel and I. S. Butler, *Trans. Faraday Soc.*, **63**, 45 (1967).

[13] (a) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc.*, **89**, 2844 (1967); (b) P. S. Braterman, R. Bau, and H. D. Kaesz, *Inorg. Chem.*, **6**, 2097 (1967).

[14] D. J. Darensbourg and T. L. Brown, *ibid.*, **7**, 959 (1968).

[15] D. J. Darensbourg, *Inorg. Chim. Acta*, **4**, 597 (1970).

[16] A. Poletti, A. Foffani, and R. Cataliotti, *Spectrochim. Acta, Part A*, **26**, 1063 (1969).

[17] W. P. Anderson and T. L. Brown, *J. Organometal. Chem.*, **32**, 343 (1971).

[18] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

[19] T. S. Piper and G. Wilkinson, *ibid.*, **2**, 38 (1956).

TABLE I

INFRARED FREQUENCIES, BAND-HALF-WIDTHS, EXTINCTION COEFFICIENTS, AND INTENSITIES FOR THE ν_{CO} VIBRATIONS IN $(C_5H_5)Fe(CO)_2X$ COMPOUNDS

Compound	Vib, cm^{-1}	$\Delta\nu_{1/2}$,[a] cm^{-1}	$10^{-2}\bar{\epsilon}$,[b] $M^{-1}\ cm^{-1}$	Intens × 10^{-4},[c] $M^{-1}\ cm^{-2}$
$(C_5H_5)Fe(CO)_2Cl$	2057.6 (A′)	11.0	19.8	7.30 ± 0.02
	2012.1 (A″)	16.0	17.5	9.69 ± 0.15
$(C_5H_5)Fe(CO)_2I$	2043.8 (A′)	12.0	19.0	7.15 ± 0.06
	2000.2 (A″)	17.3	16.7	9.63 ± 0.17
$(C_5H_5)Fe(CO)_2CN$	2120.8 (CN)	12.5	2.52	1.14 ± 0.02
	2062.2 (A′)	10.0	21.1	7.42 ± 0.15
	2018.6 (A″)	14.5	18.6	9.36 ± 0.36
$(C_5H_5)Fe(CO)_2SnCl_3$	2048.5 (A′)	11.7	21.1	7.45 ± 0.12
	2008.6 (A″)	16.0	18.6	9.26 ± 0.25
$(C_5H_5)Fe(CO)_2C(O)CH_3$	2022.6 (A′)	17.0	16.1	8.78 ± 0.06
	1962.4 (A″)	21.8	16.2	13.4 ± 0.16
$(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$	1968.1 (A′)	18.7	16.5	8.16 ± 0.06
	1907.8 (A″)	23.0	17.9	13.7 ± 0.13

[a] These are the observed half-intensity widths (apparent half-intensity widths[23]). No corrections are applied to these values since the ratio of $\Delta\nu_{1/2}$(apparent)/$\Delta\nu_{1/2}$(true) is close to unity (1.02) in these cases, thereby leading to corrections of the same magnitude as the errors involved in measuring these parameters. [b] Obtained from the least-squares slope of absorbance *vs.* concentration plots. [c] Defined as $(2.303/cl)\int_{\text{band}}\log(I_0/I)\,d\nu$, where c equals the concentrations in moles per liter and l equals the cell path length in centimeters. The errors listed are the standard deviations from least-squares analyses of the intensity *vs.* concentration plots.

$(CO)_2CN$,[18] $(C_5H_5)Fe(CO)_2C(O)CH_3$,[20] $(C_5H_5)Fe(CO)_2SnCl_3$,[21] and $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$[22] were prepared and purified by methods given in the literature. These compounds gave the following elemental analyses and melting points. *Anal.* Calcd for $(C_5H_5)Fe(CO)_2Cl$: C, 39.6; H, 2.37. Found: C, 39.3; H, 2.30 (mp 93–94.5°). *Anal.* Calcd for $(C_5H_5)Fe(CO)_2I$: C, 27.65; H, 1.69. Found: C, 27.7; H, 1.77 (mp 117–118.5°). *Anal.* Calcd for $(C_5H_5)Fe(CO)_2CN$: C, 47.35; H, 2.48; N, 6.94. Found: C, 47.4; H, 2.52; N, 6.98 (mp 127–130°). *Anal.* Calcd for $(C_5H_5)Fe(CO)_2C(O)CH_3$: C, 49.1; H, 3.6. Found: C, 49.2; H, 3.75 (mp 55.5–57°). *Anal.* Calcd for $(C_5H_5)Fe(CO)_2SnCl_3$: C, 20.9; H, 1.2. Found: C, 21.0; H, 1.30 (mp 155.5–157°). *Anal.* Calcd for $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$: C, 72.47; H, 5.13; P, 5.84 (mol wt 530). Found: C, 72.49; H, 5.11; P, 5.61 (mol wt 529; mp 144.5–146°).

Elemental analyses on these compounds were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Infrared Measurements.—The infrared spectra were recorded on a Perkin-Elmer 521 grating spectrophotometer equipped with a linear absorbance potentiometer. Samples were prepared by weighing out the solid materials on a Cahn electrobalance to ±0.01 mg. The solids were then added to volumetric flasks of appropriate size and the flasks were accurately filled with Spectrograde chloroform. Linear Beer's law plots were observed in all cases.

The compounds examined in this study were not all soluble in a noninteracting solvent, *e.g.*, hexane. Although chloroform is generally not an ideal solvent for studying CO stretching vibrations due to a strong solvent effect, no significant differences were observed in the intensity measurements in chloroform or hexane for compounds soluble in both solvents.

The spectrophotometer was calibrated in the region above 2000 cm^{-1} against the spectrum of carbon monoxide and below 2000 cm^{-1} against the spectrum of water vapor. The spectral slit width of the instrument was set at 1.8–2.0 cm^{-1}. Recordings were made on an expanded abscissa scale where 1 cm of recording paper corresponded to 5.0 cm^{-1} at a speed of 20 cm^{-1}/min.

The spectra were observed in chloroform solution using sealed 0.1-cm NaCl cells for both sample and reference. The cells were calibrated by the interference-fringes method.

The integrated intensities were determined at a number of concentrations (generally 8–10) and extrapolated to zero concentration.[23] The areas under the band envelopes were determined with a planimeter. All data were analyzed by the linear least-squares method.

Results and Discussion

In Table I stretching frequencies, band-half-widths $\Delta\nu_{1/2}$, extinction coefficients $\bar{\epsilon}$, and integrated intensities are given.[24]

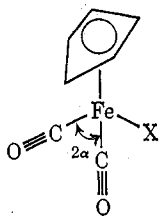

Figure 1.—Bond angle for the $Fe(CO)_2$ moiety.

The characteristic MCO group dipole moment derivative for each of the symmetry vibrations may be calculated using the equations[13b]

$$I_1^{(A')} = 2G_{tt}\cos^2\alpha(\mu'_{MCO}{}^{(1)})^2 \qquad (1)$$

$$I_2^{(A'')} = 2G_{tt}\sin^2\alpha(\mu'_{MCO}{}^{(2)})^2 \qquad (2)$$

where $I_1^{(A')}$ and $I_2^{(A'')}$ are the measured intensities $\times 10^{-4}$, G_{tt} is the inverse mass of a CO group (0.14585), $\mu'_{MCO}{}^{(1)}$ and $\mu'_{MCO}{}^{(2)}$ are the group dipole moment changes with respect to the CO stretching in each MCO group during the symmetric and asymmetric CO stretching motions, respectively, and α is one-half the angle between MCO groups (Figure 1).

Previously, attempts have been made to calculate α assuming $\mu'_{MCO}{}^{(1)}$ and $\mu'_{MCO}{}^{(2)}$ are equal.[9] As has been pointed out before this procedure is not very satisfactory.[15,25–27] Results are often however very satisfying in that good agreement with crystal structure data is observed. These results are nevertheless fortuitous, for often subtle compensating electronic effects aid in canceling out larger discrepancies in these dipole moment derivatives. There is a net demand for π-electronic charge by the CO groups from the metal in the A′ mode which is not present in the A″ mode.[14]

(20) R. B. King, *J. Amer. Chem. Soc.*, **85**, 1918 (1963).

(21) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 179 (1964).

(22) M. Y. Darensbourg, *J. Organometal. Chem.*, in press

(23) D. A. Ramsay, *J. Amer. Chem. Soc.*, **74**, 73 (1952).

(24) There are previous reports of infrared intensity measurements of some of these compounds in the literature: (a) A. N. Nesmeyanov, Y. A. Chapovskii, L. I. Denisovich, B. V. Lokshin, and I. V. Polovyanyuk, *Dokl. Chem.*, **174**, 576 (1967); J. Dalton, I. Paul, and F. G. A. Stone, *J. Chem. Soc. A*, 2744 (1969).

(25) This does not however negate the qualitative correlation between intensity and geometry as has been employed in determining, for example, cis and trans isomers of $(C_5H_5)Mo(CO)_2XL$ species.[26,27]

(26) A. R. Manning, *J. Chem. Soc. A*, 1984 (1967).

(27) F. A. Cotton and C. M. Lukehart, *J. Amer. Chem. Soc.*, **93**, 2672 (1971).

TABLE II

FORCE CONSTANTS AND GROUP DIPOLE MOMENT DERIVATIVES FOR THE ν_{CO} VIBRATIONS IN $(C_5H_5)Fe(CO)_2X$ COMPOUNDS

	Force constants[a]		Dipole moment derivatives[c]		
Compd	k_1	$k_{\rm i}$	$\mu'_{MCO}{}^{(1)}$	$\mu'_{MCO}{}^{(2)}$	$\mu'_{MCO}{}^{(1)}/\mu'_{MCO}{}^{(2)}$
$(C_5H_5)Fe(CO)_2Cl$	16.70	0.37	7.08	8.15	0.869
$(C_5H_5)Fe(CO)_2I$	16.48	0.36	7.00	8.01	0.874
$(C_5H_5)Fe(CO)_2CN$	16.88	0.44	7.13	8.01	0.890
	$(k_2 = 17.01, k_{\rm i}' = 0.24)$[b]			$(\mu'_{MCN}{}^{(3)} = 2.71)$	
$(C_5H_5)Fe(CO)_2SnCl_3$	16.59	0.33	7.15	7.97	0.897
$(C_5H_5)Fe(CO)_2C(O)CH_3$	16.01	0.48	7.76	9.58	0.810
$(C_6H_5CH_2C_2H_5)Fe(CO)_2P(C_6H_5)_3$	15.14	0.47	7.48	9.69	0.772

[a] k_1 and $k_{\rm i}$ are the stretching and interaction force constants for the CO groups, respectively. These are in units of mdyn/Å. [b] k_2 and $k_{\rm i}'$ correspond to the CN stretching and the CN–CO interaction force constants, respectively. In addition to the frequencies listed in Table I, the ^{13}CO frequency at 1986.9 cm^{-1} was employed in determining the four force constants in the $(C_5H_5)Fe(CO)_2CN$ molecule by the iterative procedure.[15] The frequency fit was ±0.8 cm^{-1} or 0.039%. The L_{ij} matrix elements for the mixing of the A′ modes of ν_{CN} and ν_{CO} were $L_{11} = -L_{22} = 0.3656$ and $L_{12} = L_{21} = 0.1453$. [c] These were computed assuming an α value of 45°. See text for variations as a function of α.

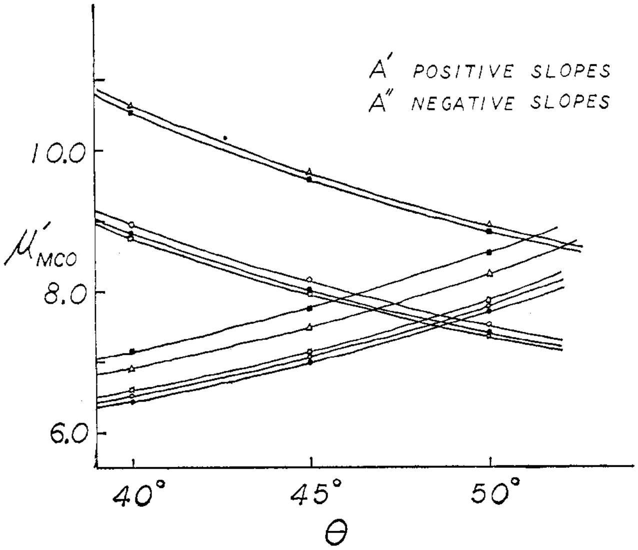

Figure 2.—Angular dependence of $\mu'_{MCO}{}^{(1)}$ and $\mu'_{MCO}{}^{(2)}$: ○ $(C_5H_5)Fe(CO)_2Cl$; ●, $(C_5H_5)Fe(CO)_2I$; □, $(C_5H_5)Fe(CO)_2CN$ or $(C_5H_5)Fe(CO)_2SnCl_3$; ■, $(C_5H_5)Fe(CO)_2C(O)CH_3$; △, $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$. Negative slopes are for $\mu'_{MCO}{}^{(2)}$ and positive slopes correspond to $\mu'_{MCO}{}^{(1)}$.

This demand increases as the CO bond stretches, since the π^* orbitals of the CO group decrease in energy. Since the intensity is largely dependent on the π-electronic charge in the MCO grouping, the expected order of dipole moment derivatives is $\mu'_{MCO}{}^{(1)} < \mu'_{MCO}{}^{(2)}$. Vibronic contributions which are a function of the demand made for π electrons during the CO stretching motions may lead to $\mu'_{MCO}{}^{(1)} \geq \mu'_{MCO}{}^{(2)}$.[14,15] These vibronic contributions have been shown to be very useful in the understanding of the bonding of the substituent ligands to the transition metal.[14,15,28]

It is for these reasons that we wish to calculate dipole moment derivatives as a function of the angle (α) instead of calculating α by assuming $\mu'_{MCO}{}^{(1)} = \mu'_{MCO}{}^{(2)}$. Figure 2 shows plots of $\mu'_{MCO}{}^{(1)}$ and $\mu'_{MCO}{}^{(2)}$ as a function of the angle (α). As can easily be seen from these plots in order for $\mu'_{MCO}{}^{(1)} = \mu'_{MCO}{}^{(2)}$ in all the compounds studied, α must be greater than 49°. Although no crystal structure data are available on the $(C_5H_5)Fe(CO)_2X$ compounds where X = halogens, CN, or $C(O)CH_3$, data exist for the $SnCl_3$,[29a] $SnBr_3$,[29a] and $Sn(C_6H_5)_3$[29b] derivatives and for $(C_5H_5)Mn(CO)_3$[29c] in which the MCO grouping angles are close to 90° or α equals 45°. Since all the substituent groups (L) studied here are sterically as large or larger than carbon monoxide it is expected that α will be close to 45°. Therefore, the dipole moment derivatives listed in Table II which are calculated assuming an α value of 45° are upper limits for the $\mu'_{MCO}{}^{(1)}$ values and lower limits for the $\mu'_{MCO}{}^{(2)}$ values.

It is possible to conclude from the substantially greater value of $\mu'_{MCO}{}^{(2)}$ over $\mu'_{MCO}{}^{(1)}$ that there is not a sizable vibronic contribution from the cyclopentadienyl ligand. Since vibronic contributions are related to the extent of back-bonding in the metal–ligand bond, this in turn leads to the conclusion that there is little back-bonding in the metal–cyclopentadienyl moiety. This conclusion is in agreement with the net positive charge on the carbon atoms of the cyclopentadienyl group in these types of compounds obtained *via* photoelectron spectroscopy.[4] Vibronic contributions from the cis X ligands are expected to be small and therefore have little effect on the intensities.[30] This is illustrated in the fact that the nature of the X group does not affect the $\mu'_{MCO}{}^{(1)}/\mu'_{MCO}{}^{(2)}$ ratio significantly.[31]

The intensity results indicate that the extent of Fe–CO π bonding in these $(C_5H_5)Fe(CO)_2X$ compounds and therefore the net electronic effect of the X ligands are approximately the same for X = Cl, I, CN, and $SnCl_3$,[32] whereas there is a significant increase in the Fe–CO π bonding upon going to $(C_5H_5)Fe(CO)_2C(O)CH_3$ or $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$.

A correlation exists between $\Delta\nu_{1/2}$ and ν_{CO} in the

---

(28) D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chim. Acta*, **5**, 247 (1971).

(29) (a) R. F. Bryan, P. T. Greene, G. A. Melson, and P. F. Stokely, *J. Chem. Soc. D*, 722 (1969); (b) R. F. Bryan, *J. Chem. Soc. A*, 192 (1967); (c) A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, **16**, 118 (1963).

(30) This vibronic contribution may become significant if very good π-acceptor (X) ligands are studied. Although $SnCl_3$ is considered to be a good π acceptor, $\mu'_{NCO}{}^{(1)}/\mu'_{NCO}{}^{(2)}$ is about the same as that of the halogens. No explanation for this observation can be offered at this time. Professor W. P. Anderson of the University of Delaware has completed a comprehensive study (to be submitted for publication) of $(C_5H_5)Mn(CO)_2L$ compounds in which no substantial vibronic contributions are observed for π-bonding ligands, L.

(31) The slightly smaller ratios in the $(C_5H_5)Fe(CO)_2C(O)CH_3$ and $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$ compounds may be a result of steric factors leading to a somewhat smaller angle α. Alternatively, this may be an electronic effect. The demand made for π-electron density during the CO vibrations is dependent on the extent of M–CO π interactions. Since this type interaction is greater in these compounds, the demand made during the A′ vibration will be greater here and thereby could explain the smaller dipole moment derivatives for the A′ mode as compared with the A″ mode.

(32) The intensity of the A′ vibration in $(C_5H_5)Fe(CO)_2CN$ will be slightly larger than that reported in Table I due to coupling with ν_{CN}. This, however, will not alter the conclusions reached here significantly. In this respect, the low intensity of ν_{CN} as compared with ν_{CO} is indicative of the much stronger π-acceptor ability of carbon monoxide.

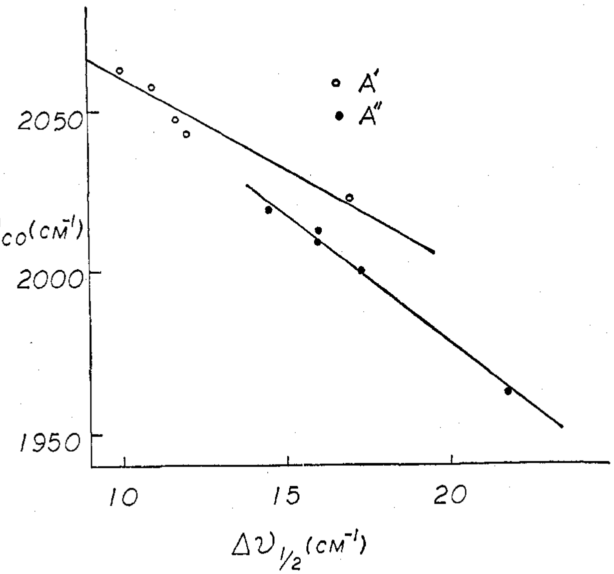

Figure 3.—Correlation between $\Delta\nu_{1/2}$ and ν_{CO} in $(C_5H_5)Fe(CO)_2X$ compounds.

$(C_5H_5)Fe(CO)_2X$ series.[33] Figure 3 contains plots of linear relationships between $\Delta\nu_{1/2}$ *vs.* ν_{CO} for both the A′ and A″ vibrational modes. The magnitude of $\Delta\nu_{1/2}$ is expected to be related to the degree of solvent interactions with the MCO dipoles.[34] This interaction is presumably dependent on the extent of polarization of the carbonyl groups in addition to steric factors about these groups. Since there are no significant deviations from linearity for such large ligands as trichlorotin, steric factors do not appear to be important in these cases. These observations are therefore in agreement with intensity studies, indicating an increase in the electric dipole of the MCO grouping as the CO stretching frequency decreases.

The interpretations of the intensities in the $(C_5H_5)Fe(CO)_2X$ derivatives are consistent with recent calculations of the infrared intensities in *fac*-$M(CO)_3L_3$ molecules, *e.g.*, $(C_5H_5)Mn(CO)_3$ or $(C_6H_6)Cr(CO)_3$, by Anderson and Brown[17] employing a molecular orbital model. These authors conclude that the asymmetric: symmetric intensity ratio should be a very sensitive measure of the importance of back-bonding in compounds of this type. Analogous arguments should apply to the A′ and A″ vibrational modes in the $(C_5H_5)Fe(CO)_2X$ species. Indeed, similar calculations by Anderson[35] on the $(C_6H_6)Cr(CO)_2L$ species clearly indicate this to be the case.

Acknowledgments.—The author is most grateful to Drs. T. L. Brown and W. P. Anderson for a preprint of their manuscript prior to publication. He also thanks Dr. W. P. Anderson for helpful discussions during the course of these studies and Dr. M. Y. Darensbourg for samples of several of the compounds mentioned in this work. Financial support from the Petroleum Research Fund administered by the American Chemical Society is also gratefully acknowledged.

[33] This trend also exists for the $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$ complex.

[34] L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, **12**, 53 (1970).

[35] W. P. Anderson, private communication of unpublished results.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN 53706

Reactions of Mono- and Bis(organo)phosphines with Iron Carbonyls

BY P. M. TREICHEL,* W. K. DEAN,[1] AND W. M. DOUGLAS

Received October 8, 1971

Reactions of $Fe_2(CO)_9$ and various primary and secondary phosphines at 25° give the phosphine–iron tetracarbonyl species $Fe(CO)_4$phos (phos = CH_3PH_2, $C_6H_5PH_2$, $P(C_6H_5)_2H$, $P(p\text{-}CH_3C_6H_4)_2H$, $P(CH_3)_2H$, $P(C_2H_5)_2H$, $P(C_6H_5)(CH_3)H$) as major products. A small amount of the dinuclear complexes $Fe_2(CO)_6(PRR')_2$ usually accompanies the formation of the $Fe(CO)_4$phos compounds. In the secondary phosphine–$Fe_2(CO)_9$ reactions a third product $Fe_2(CO)_6(PRR')H$ is also observed; this complex, which has a hydride bridging two metals, is better obtained from $Fe(CO)_4(PR_2H)$ by deprotonation with butyllithium followed by addition of $Fe_2(CO)_9$. On heating or on irradiation $Fe(CO)_4$phos species are converted to the dinuclear complexes $Fe_2(CO)_6(PR_2)_2$. When reactions of $Fe(CO)_5$ and $C_6H_5PH_2$ are run at 190°, the only product is $Fe_3(CO)_9(PC_6H_5)_2$. Several derivatives of this complex were obtained, by substitution of trimethyl phosphite for one, two, or three carbonyls.

Introduction

Reactions of iron carbonyls ($Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$) with tertiary phosphines have been studied in considerable detail.[2] More recently analogous reactions with phosphine[3] and with several secondary phosphines have also been reported.[4,5] These latter reactions, when run using moderate conditions (80°),[4a] yield products derived from simple substitution of one or two carbonyls by phosphines. Using higher reaction temperatures, dinuclear complexes are formed with loss of hydrogen from the phosphine. Two different stoichiometries are reported; $Fe_2(CO)_6[P(C_6H_5)_2]_2$ is obtained from $Fe_3(CO)_{12}$ and $P(C_6H_5)_2H$ in refluxing toluene,[4b] and the unusual $Fe_2(CO)_6[P(CF_3)_2]_2H_2$ is reported to be formed from $Fe(CO)_5$ and $P(CF_3)_2H$ in toluene.[5]

Actually the isolation of carbonyl complexes of phosphine and of secondary phosphines with other metals is not uncommon. The stability of such complexes to loss of hydrogen and to consequent formation of phos-

[1] National Science Foundation Predoctoral Fellow.

[2] T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1966).

[3] E. O. Fischer, E. Louis, W. Bathelt, and J. Müller, *Chem. Ber.*, **102**, 2547 (1969).

[4] (a) J. G. Smith and D. T. Thompson, *J. Chem. Soc. A*, 1694 (1967); (b) M. Cooke, M. Green, and D. Kirkpatrick *ibid.*, 1507 (1968).

[5] R. Dobbie and D. Whittaker, *J. Chem. Soc. D*, 796 (1970).