Table II. Conversion[a] to Products as a Function of Photocatalyst in the Presence of 0.5 M Ac_2O for 1 M $PhNO_2$ and 1 M NMP in Benzene after 15 h of Irradiation[b]

Porphyrin[c]	PhNHCOMe	PhNHOCOMe	*N*-Methylpyrrole
ZnTPP	3.84	0.50	5.50
$Sn^{IV}TPPCl_2$	14.80	2.50	17.70

[a] Percent of initial nitrobenzene. [b] λ_{excit} >500 nm. [c] 5×10^{-4} M porphyrin.

Table III. Concentration of Photocatalyst[a] in Its Steady-State[b] as a Function of Donor and Acceptor Substrates

Donor	Acceptor	TPC, %	IsoB, %
Triethylamine, 1 M	Nitrobenzene[c], 1 M	60	40
N-Methylpyrrolidine, 1 M	Nitrobenzene,[c] 1 M	0	100
N-Methylpyrrolidine, 1 M	*p*-Dinitrobenzene,[d] 0.1 M	50	50

[a] 5×10^{-4} M $Sn^{IV}TPPCl_2$ in benzene. [b] 1 h of irradiation. [c] λ_{excit} >500 nm. [d] λ_{excit} >550 nm.

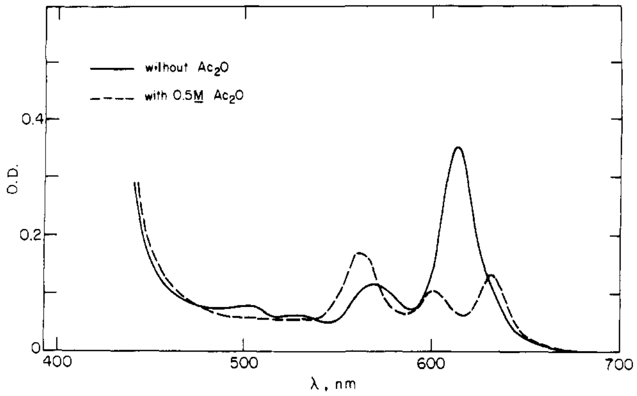

Figure 2. Optical spectra of photocatalyst ($Sn^{IV}TPPCl_2$) steady state with and without Ac_2O.

as a cocatalyst in the photocatalytic reaction. Table II gives the results. The reduction step is relatively unaffected by the addition of acetic anhydride. The reduction products are mostly acetanilide (PhNHCOMe) and some ester (PhNHOCOMe).

In Table III is shown how a steady-state concentration of chlorin and isobacteriochlorin establishes itself soon after the start of the photocatalytic run. This steady state depends on the donor and acceptor properties of the substrates. Replacement of triethylamine by the better donor NMP moves the steady state entirely to isobacteriochlorin, while replacement of $PhNO_2$ by the better acceptor, *p*-dinitrobenzene, moves it back toward a chlorin-isobacteriochlorin mixture. In Figure 2 is shown how the addition of Ac_2O, which accelerates the phooxidation reaction, moves the steady state from isobacteriochlorin toward a chlorin-porphyrin mixture.

ZnTPP in the absence of Ac_2O is inactive as a photocatalyst, but from Table II it can be seen that in the presence of Ac_2O it is active. Because ZnTPP is not photoreduced by tertiary amines the cocatalytic effect of Ac_2O cannot be attributed to an acceleration of the photooxidation step in this case and the mechanism must be different.

The mechanism of porphyrin photocatalysis in photosynthesis is of great importance. Our observations prove that metalloporphyrins can act as photocatalysts in vitro and produce chemical conversions under specific conditions. Work is in progress to study the mechanism of these reactions in more detail and to search for other metalloporphyrins with photocatalytic properties.

References and Notes

(1) J. Manassen, *Cat. Rev. Sci. Eng.*, **9**, 223-243 (1974).
(2) D. Mauzerall, *J. Am. Chem. Soc.*, **82**, 1832, 2601 (1960); **84**, 2437 (1962).
(3) G. R. Seely and M. Calvin, *J. Chem. Phys.*, **23**, 1068 (1955).
(4) F. M. Huennekens and M. Calvin, *J. Am. Chem. Soc.*, **71**, 4031 (1949).
(5) G. R. Seely, *J. Phys. Chem.*, **73**, 117 (1969).
(6) J.-H. Fuhrhop and T. Lumbantobing, *Tetrahedron Lett.*, **32**, 2815 (1970).
(7) D. G. Whitten, J. C. You, and F. A. Carroll, *J. Am. Chem. Soc.*, **93**, 2291 (1971).
(8) A 900-W xenon lamp (Osram XBO ofr.) in a Schoeffel Instrument Corp. LH151N lamp housing and Corning cut-off filters. Progress of the reaction and formation of products was studied by VPC (on a silicon nitrile rubber Xe-60 column).
(9) For the spectrum of $Sn^{IV}TPPCl_2$ see G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Am. Chem. Soc.*, **73**, 4315 (1951), and M. O'Rourke and C. Curran, *ibid.*, **92**, 1501 (1970). For the spectrum of $Sn^{IV}TPCCl_2$, see G. D. Dorough and F. M. Huennekens, *ibid.*, **74**, 3974 (1952). The spectrum of $Sn^{IV}TPIsoBCl_2$ was not previously reported in literature. It is similar to that of tin(IV) octaethylisobacteriochlorin: D. G. Whitten and J. C. N. You, *Tetrahedron Lett.*, **36**, 3077 (1969). The photochemical synthesis of $Sn^{IV}TPIsoBCl_2$ will be published separately; NMR of the product proves the assigned structure.
(10) Y. Harel, J. Manassen, and H. Levanon, *Photochem. Photobiol.*, **23**, 337 (1976).

Y. Harel, J. Manassen*
Department of Plastics Research
The Weizmann Institute of Science
Rehovot, Israel
Received March 9, 1977

Intrinsic Acidities of Ketones and Aldehydes. Bond Dissociation Energies and Electron Affinities

Sir:

Recently[1] we reported the gas phase acidities of a number of carbon acids RH. These were obtained from measurement of the gas phase equilibria 1.

$$R_1H + R_2^- = R_1^- + R_2H \qquad (1)$$

The data included the acidities of several ketones and diketones. The present communication reports new measurements for several ketones and aldehydes. The new data, when combined with Brauman's[2] recent results on the electron affinities of the corresponding enolate radicals R, reveal some interesting regularities in the changes of the gas phase acidities of RH, the electron affinities of R, and the bond dissociation energies of R-H.

The results from the measured equilibria 1 are displayed in Figure 1. The measurements were made in a high pressure mass spectrometer,[3] using procedures similar to those described earlier.[1]

The free energy changes determined at 500 K, $\Delta G_1°(500) = RT \ln K_1$ shown in Figure 1, include multiple thermodynamic cycles which are consistent to better than ±0.3 kcal/mol. The $\Delta G_2°(500)$ values relating the acidities to that of the primary standard HCl (eq 2) were obtained via pyrrole whose $\Delta G_2°(500)$ was determined in separate measurements.[1,4] The $\Delta G_2°(600)$ values for pyrrole, acetophenone, and acetone determined in the earlier publication[1] (at 600 K) are also shown in Figure 1. As can be seen the present values for pyrrole and acetophenone are very close to those obtained earlier. However the new $\Delta G_2°(500)$ value for acetone is some 2 kcal/mol higher.[5] From $\Delta G_2°$, $\Delta H_2°$ can be evaluated by calculating[7] $\Delta S_2°$. In turn the $\Delta H_2°$ combined with the known $D(\text{H-Cl}) - EA(\text{Cl}) = 20$ kcal/mol[8,9] leads to $D(\text{R-H}) - EA(\text{R})$.

$$RH + Cl^- = R^- + HCl \qquad (2)$$

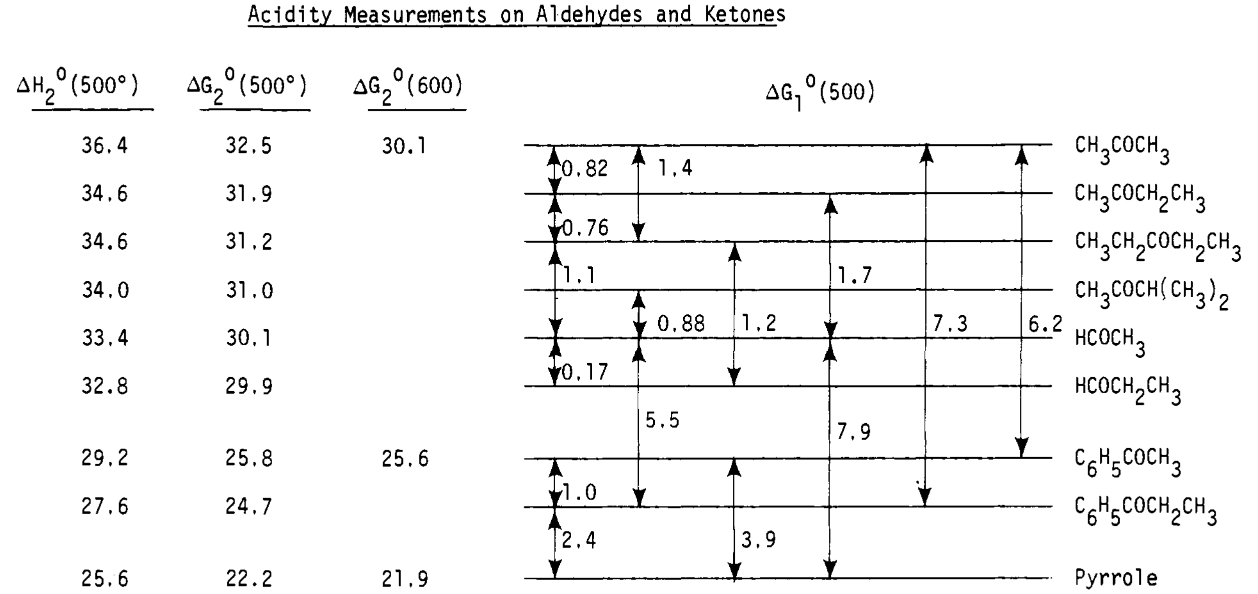

Figure 1. Summary of gas phase acidity measurements. Numbers beside double arrows represent directly measured $\Delta G_1°(500) = -RT \ln K_1$ for reaction 1: $R_1H + R_2^- = R_1^- + R_2H$ measured at 500 K. R_1H is the compound on the upper end of the double arrow. $\Delta G_2°(500)$ values, given in second column on the left, are values for reaction 2: $RH + Cl^- = R^- + HCl$ relating present acidities to the primary standard HCl. $\Delta G_2°(600)$ values are results obtained in previous publication.[1]

Results for the electron affinities of the enolate radicals R obtained by Brauman[2] and D − EA values from the present determinations are shown in Table I. The agreement of the present results with literature data can be examined for acetone and 2-butanone. The present D − EA of 56.2 for acetone, when combined with the EA of 40.6 kcal/mol of Brauman,[2] gives D of 96.8 kcal/mol, while the literature value of D is 98.0 kcal/mol.[10] For $CH_3COCH(CH_3)$-H, the D − EA of 54.6 kcal/mol combined with EA of 38.6 kcal/mol[2] gives D of 93.2 kcal/mol, while Benson data[11] provide a D of 92.3 kcal/mol. In both cases the agreement is better than the expected errors in the measurements.

The top four compounds in Table I, $HCOCH_2$-H, CH_3COCH_2-H, $C_6H_5COCH_2$-H, and CF_3COCH_2-H, differ only in the substituent to the carbonyl carbon. The corresponding bond energies, 95.1, 96.8, 96.8, and 96.2 kcal/mol, are remarkably constant. On the other hand, the electron affinities change a great deal. For example an increase of 19 kcal/mol occurs from CH_3 to CF_3. Thus, for carbonyl carbon substituents, the acidity follows the electron affinity, which increases with increasing electron-withdrawing power of the substituent.

The series $HCOCH(CH_3)$-H, $CH_3COCH(CH_3)$-H, and $C_2H_5COCH(CH_3)$-H also differs in the nature of the carbonyl carbon substituent and shows changes which exactly parallel those considered above.

Considering specifically alkyl substituents on the carbonyl carbon, we find that the change from H to CH_3 decreases the electron affinity and increases D(R-H); both these changes are small but they add to produce a significant decrease of the acidity. The increase of acidity and electron affinity between methyl and ethyl is very small, but further increase of the size of the alkyl group to *tert*-butyl leads to a noticeable increase of electron affinity and acidity. Analogous alkyl substituent effects were previously found for aliphatic carboxylic acids, whose acidities increase in the order[12] acetic, propionic, butyric, formic acid, and the acetylenes, whose acidities increase in the order[13,14] CH_3C_2-H, $C_2H_5C_2$-H, n-$C_3H_7C_2$-H, HC_2-H. Significantly the position in which the substituent is changed involves a carbon atom that is conjugated to the negative charge center(s). As suggested by Brauman,[14] when H is replaced with methyl,[15] the dipole of the CH_3 group destabilizes the negative charge[16] and decreases the electron affinity.[17] Increase of the alkyl group does not lead to an appreciable increase of the alkyl dipole; however, the increasing polarizability of the alkyl group leads to increasing stabilization of the ion.

Table I. Acidities, Electron Affinities, and Bond Dissociation Energies[a]

Compd	D(R-H) − EA(R)[b]	EA(R)[c]	D(R-H)[d]
$HCOCH_2$-H	53.4	41.7 ± 1.4	95.1
CH_3COCH_2-H	56.4	40.6 ± 1.3	97.0 (98.0 ± 2)[e]
$C_6H_5COCH_2$-H	49.2	47.6 ± 1.8	96.8
CF_3COCH_2-H	36.7	59.5 ± 2.9	96.2
($CH_3CH_2COCH_2$-H)	(56.1)[f]	40.4 ± 1.3	(96.5)[f]
(t-$C_4H_9COCH_2$-H)	(54.0)[f]	42.5 ± 1.5	(96.5)[f]
$HCOCH(CH_3)$-H	52.8	38.9 ± 1.2	91.7
$CH_3COCH(CH_3)$-H	54.6	38.6 ± 1.2	93.2 (92.3 ± 1.4)[e]
$C_2H_5COCH(CH_3)$-H	54.6	38.8 ± 1.2	93.4

[a] All values in kilocalories/mole. [b] From $\Delta H_2°$ for proton transfer equilibria: $R_1^- + R_2H = R_1H + R_2^-$ obtained from corresponding $\Delta G_2°$ and estimates of entropy change $\Delta S_2°$. Estimated error ±2 kcal/mol in absolute values. [c] Zimmerman, Reed, and Brauman[2] photodetachment measurements. [d] Evaluated from D(R-H) − EA(R)[b] and EA(R),[c] except where otherwise indicated. [e] Solly, Golden, and Benson,[10,11] kinetic determinations of D(R-H). [f] Estimates, based on assumption that D(R-H) = 96.5 kcal/mol.

The introduction of methyl on the carbon carrying the acidic hydrogen in the carbonyl compounds decreases the electron affinity. Thus EA($HCOCH_2$) is bigger than EA($HCOCHCH_3$) by ~3 kcal/mol and a similar difference occurs also for EA in CH_3COCH_2 and $CH_3COCHCH_3$. However, the same substitution decreases D(R-H) since the R-H bond changes from a primary to secondary bond. This favorable change is larger and offsets the decrease of electron affinity. This results in an increase of acidity. It is interesting to note that the bond energy changes with methyl substitution are $HCOCH_2$-H − $HCOCH(CH_3)$-H = 3.4 kcal/mol and

CH_3COCH_2-H − $CH_3COCH(CH_3)$-H = 3.6 kcal/mol. This is very close to the change CH_3CH_2-H − $CH_3CH(CH_3)$-H = 3.5 kcal/mol.[20] The correspondence of these energy differences may be expected, since the introduction of a carbonyl group does not seem to change the α C-H bond strengths; thus the strength of CH_3CH_2-H = 98 kcal/mol, while that of CH_3COCH_2-H ≈ 97 kcal/mol.

Acknowledgement. The present work was supported by Grants from the Canadian National Research Council.

References and Notes

(1) T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 3399 (1976).
(2) A. H. Zimmerman, K. J. Reed, and J. I. Brauman, *J. Am. Chem. Soc.*, in press.
(3) A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Am. Chem. Soc.*, **94**, 7628 (1972).
(4) J. B. Cumming and P. Kebarle, *J. Am. Chem. Soc.*, in press.
(5) The earlier measurement[1] of $\Delta G_2°$ is believed to be less accurate. It was based on equilibria measurements involving diphenylmethane and 1,4-pentadiene. As noted in the earlier publication,[1] these equilibria were difficult to measure. The proton-transfer reaction involving the extensively delocalized $(Ph)_2CH^-$ is slow.[6] The equilibrium measurement involving 1,4-pentadiene was subsequently found to be unreliable since the protonation of the anion $(CH_2CH{-})_2CH^-$ leads to 1,4-pentadiene *and* 1,3-pentadiene. A restudy of the 1,4-pentadiene–1,3-pentadiene system will be published (J. B. Cumming and P. Kebarle).
(6) W. E. Farneth and J. I. Brauman, *J. Am. Chem. Soc.*, **98**, 7891 (1976).
(7) The entropy changes in the proton transfer reaction $2Cl^- + HR = HCl + R^-$ involving the carbonyl compounds are mostly due to appearance of two rotational degrees of freedom in change $Cl^- \rightarrow HCl$ and the appearance of a barrier to internal rotation in the enolate anion, due to formation of the (partial) double bond $C{=}C{-}O^-$. The net effect is $\Delta S_2 \approx 6$ cal/deg or a $T\Delta S_2 \approx 3$ kcal/mol at 500 K. A full account of the entropy corrections concerning all acid determinations done in this laboratory is given in ref 4.
(8) "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-3, U.S. Department of Commerce, 1968.
(9) R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38**, 1540 (1963).
(10) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 11 (1970).
(11) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 381 (1970).
(12) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 4050 (1973).
(13) R. T. McIver, J. Bartmess, and J. S. Miller, paper presented at Fifth Structure-Energy Relationships Conference, Santa Barbara, Calif., 1977.
(14) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **93**, 4315 (1971).
(15) The methyl group needs not be "electron donating" (relative to H), since a net transfer of electrons away from methyl, probably, does not occur.[16]
(16) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(17) The decrease in electron affinity upon substitution of methyl for hydrogen at the acidic center is not restricted to substitution at an unsaturated carbon, as is discussed here, but is also evident for the saturated couple H_2O and CH_3OH. EA(HO·) = 42 kcal/mol[18] > EA(CH_3O·) = ~39 kcal/mol.[19]
(18) L. M. Branscomb, *Phys. Rev.*, **148**, 11 (1966).
(19) R. T. McIver and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 4323 (1974).
(20) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

J. B. Cumming, P. Kebarle*
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2G2
Received May 2, 1977

Synthesis, Characterization, and Crystal Structure of $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$, a Species Containing an Ortho-Dimetalated Phenyl Ring Resembling a Meisenheimer Complex

Sir:

The fission reactions of a wide range of organotin derivatives (and other organo (group 4B) species of general formula R_3MX (M = Si, Ge, Sn)) have been noted as providing synthetic routes for the formation of novel metal carbonyl derivatives.[1] In particular, a variety of organo-nitrogen ligands have been introduced as bridging ligands, yielding such species as $Mn_2(CO)_8[\mu_2\text{-}N{=}NPh]_2$,[2] $Mn_2(CO)_7[\mu_2\text{-}N{=}C(CF_3)_2]_2$,[3] and $HRu_3(CO)_{10}[\mu_2\text{-}C{=}NMe_2]$.[4] We now report the extension of these studies to the reaction of the organotin ylide,[5] $(Me_3Sn)_2C{=}PPh_3$ (made conveniently[6] from dimethylaminotrimethyltin and methyltriphenylphosphonium bromide) and dodecacarbonyltriiron, $Fe_3(CO)_{12}$). While we had expected to produce a molecule containing a simple bridging ylide ligand, the species actually isolated is $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$, produced by the reaction shown in eq 1.

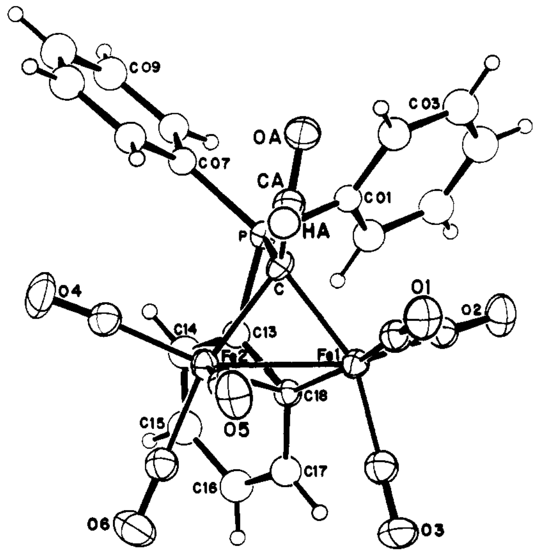

Figure 1. Stereochemistry of molecule A in the $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$ crystal. (ORTEP diagram; 30% probability ellipsoids for all nonhydrogen atoms.) The aldehyde group is defined by atoms C(A), O(A), and H(A).

$$(Me_3Sn)_2C{=}PPh_3 + Fe_3(CO)_{12} \rightarrow Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)] + CO + (Me_3Sn)_2Fe(CO)_4 \quad (1)$$

The identity of this unusual molecule has been determined by a variety of physical techniques,[7] culminating in a full three-dimensional crystal structure analysis. The infrared spectrum of this material contains six bands attributable to terminal carbonyl ligands (at 2050, 2023, 2019, 1989, 1980, and 1975 cm^{-1}) and one band (1626 cm^{-1}) assigned to an aldehydic C=O stretch. The ^1H NMR spectrum contains peaks due to the aromatic protons and a doublet at δ 9.35 and 9.02 ($^3J(^1H\text{-}^{31}P)$ = 33.57 Hz), assigned to the aldehydic proton. The most abundant peak in the parent-ion multiplet of the mass spectrum is at *m/e* 582, consistent with the formula $^{12}C_{26}{}^1H_{15}{}^{56}Fe_2{}^{16}O_7{}^{31}P^+$; in addition, there are characteristic patterns at intervals of 28 mu, consistent with the stepwise loss of six carbonyl ($^{12}C^{16}O$) ligands.

X-ray diffraction data were collected with a Syntex P2$_1$ diffractometer[8] and were corrected for absorption (μ = 13.13 cm^{-1}). The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a = 18.886 (6) Å, b = 15.898 (4) Å, c = 17.699 (5) Å, β = 115.04 (2) °, V = 4814 (2) Å^3, ρ_{obsd} = 1.613 (5) g cm^{-1} and ρ_{calcd} = 1.606 g cm^{-1} for mol wt 582.073, and Z = 8. The structure was solved by symbolic addition and refined by full-matrix least-squares methods (Fe, P, O, and ylide C anisotropic; phosphine and carbonyl carbon atoms isotropic; hydrogen atoms in calculated positions) to final discrepancy indices of R_F 5.0% and R_{wF} 4.4% for the 4070 independent reflections with $I \geqslant \sigma(I)$ and $2\theta \leqslant 40°$ (Mo Kα radiation). All atoms (including all 15 hydrogen atoms in each molecule) were located. The crystallographic asymmetric unit consists of two chemically equivalent molecules (termed molecule A and molecule B) of composition $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$. The molecular stereochemistry is depicted in Figure 1.

(In subsequent discussion the bond length or angle for molecule A will be given first; that for molecule B will appear