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.

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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.

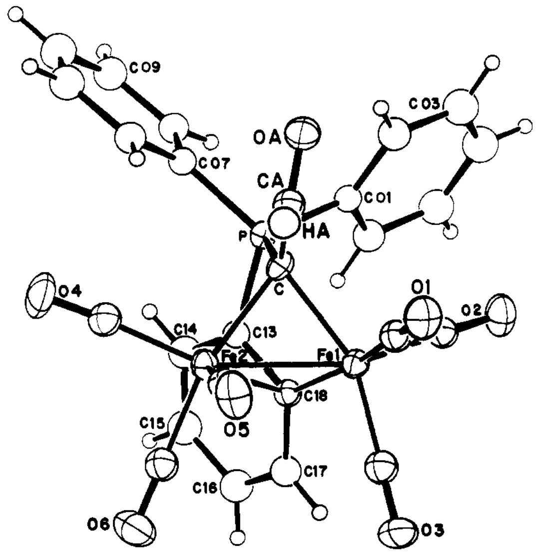

Figure 1. Stereochemistry of molecule A in the $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$ crystal. (ORTEP diagram; 30% probability ellipsoids for all nonhydrogen atoms.) The aldehyde group is defined by atoms C(A), O(A), and H(A).

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

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 ($^3J(^1H-^{31}P)$ = 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

Table I. C–C Distances within the Ortho-Dimetalated Ring

Bond	Bond length, Å	
	Molecule A	Molecule B
C(18)–C(13)	1.424 (8)	1.437 (9)
C(13)–C(14)	1.427 (8)	1.432 (8)
C(14)–C(15)	1.364 (9)	1.373 (10)
C(15)–C(16)	1.381 (10)	1.390 (10)
C(16)–C(17)	1.362 (9)	1.365 (9)
C(17)–C(18)	1.446 (8)	1.448 (9)

in parentheses immediately following the entry for molecule A.)

The molecule contains an $(OC)_3Fe-Fe(CO)_3$ unit, in which the Fe–Fe distance is 2.471 (1) Å (2.466 (1) Å), which is doubly bridged by a $C(CHO)P(Ph_2C_6H_4)$ ligand bonding from the original ylide carbon atom (labeled "C" in Figure 1) and the ortho-carbon atom of one phenyl ring (designated C(18)). The angle between the Fe(1)–C–Fe(2) and Fe(1)–C(18)–Fe(2) planes is 106.70° (106.45°). The $C(CHO)P(Ph_2C_6H_4)$ ligand is formally derived by attack of a carbonyl fragment at the ylide carbon atom, followed by (or in concert with) transfer of an ortho hydrogen from the PPh_3 moiety.

In valence bond terms, the phosphorus atom is best thought of as the center for a phosphonium cation. Thus, P–Ph distances average 1.803 Å, the P–C(13) distance is 1.785 (6) Å (1.784 (6) Å), and the P–C (ylide) distance is 1.748 (6) Å (1.749 (6) Å). The formal positive charge on the phosphorus atom is counterbalanced by a negative charge delocalized over the C(13)–C(14)–C(15)–C(16)–C(17) system; the conjugation around the six-membered ring is broken by dimetallation of the ortho position (C(18)), making this ring approximate that of a Meisenheimer complex found in nucleophilic aromatic substitution reactions. In keeping with this view, the ortho-dimetalated phenyl ring is only slightly distorted from planarity, with C(18) being displaced some 0.031 (6) Å (0.037 (6) Å) from the plane defined (root mean square deviation 0.004 Å) by atoms C(13) through C(17). In addition to this, the internal angle at C(18) is reduced toward the regular tetrahedral angle, having a value of 114.3 (5)° (113.4 (5)°). Distances within this system are listed in Table I.

The Fe(1)–C(18)–Fe(2) bridge is rather asymmetric, the Fe(1)–C(18) distance being 2.001 (6) Å (1.986 (6) Å), i.e., some 0.15–0.20 Å shorter than the Fe(2)–C(18) bond length of 2.159 (5) Å (2.185 (6) Å). The Fe(1)–C(18)–Fe(2) angle is 72.76 (19)° (72.29 (20)°). In contrast to this, the Fe(1)–C(ylide)–Fe(2) bridge is fairly regular, with Fe(1)–C(ylide) 2.037 (6) Å (2.036 (6) Å), Fe(2)–C(ylide) 2.047 (6) Å (2.052 (6) Å), and ∠Fe(1)–C–Fe(2) 74.44 (19)° (74.19 (20)°). The aldehydic function is normal with C(ylide)–C(A) 1.448 (8) Å (1.453 (9) Å), C(A)–O(A) 1.218 (9) Å (1.220 (9) Å), and ∠C–C(A)–O(A) 125.8 (6)° (124.5 (6)°).

Finally, it should be noted that, despite the steric availability of a third bridging site between the metal atoms, there is no bridging hydride ligand. This has been confirmed by detailed difference-Fourier syntheses in addition to the mass spectrometric and ^1H NMR results reported above.

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Supplementary Material Available: Tables of x-ray crystallographic data (2 pages). Ordering information is given on any current masthead page.

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The Relationship between Substituent Effects on Energy and on Charge from ab Initio Molecular Orbital Theory[1]

Sir:

Ab initio molecular orbital calculations at the minimal basis set STO-3G level have proven successful in reproducing the experimental gas phase energies (relative proton affinities) for a variety of *isodesmic* proton transfer equilibria.[2-5] With substituted methylamines,[2] for example,

$$XCH_2NH_3^+ + HCH_2NH_2 \rightleftharpoons XCH_2NH_2 + HCH_2NH_3^+ \qquad (\Delta E^\circ_{\text{calcd}} \simeq \Delta H^\circ_{\text{obsd}}) \quad (1)$$

Ab initio calculations of charge densities have been shown also to successfully correlate ^{13}C NMR shifts[6] and infrared intensities[7] in monosubstituted benzenes. We wish now to report the preliminary findings from this theory regarding substituent effects on the protonic charge of the cation and the corresponding energy charge for proton transfer. This is a matter of substantial importance since many of the concepts of organic chemistry are described in terms of the charge-releasing or -donating properties of substituents. Included are the σ-inductive effect, π-inductive effects, and resonance interactions.[7] Only the field effect, the electrostatic interaction of a substituent dipole with a distant dipolar or charge reaction site, is expressed in energy terms. While some properties such as NMR chemical shifts are often thought of as dependent on charge,[8] the vast majority of substituent effect correlations (e.g., of equilibria and reaction rates) involve energy, not charge measurements.

Implicit in the interpretation of fundamental energy changes in terms of the movement of charge is the assumption that the two quantities are directly related to one another. This assumption was specifically incorporated into the early theoretical treatment of aromatic acid dissociation energies by Roberts and Jaffe.[9] Much more recently, an empirical model of proton affinities has been postulated which assumes a direct relationship between this parameter and hydrogen charge density.[10] However, surprisingly little direct evidence is available on this point. Calculations at the INDO level have shown[11] that the charge on the carboxylic acid hydrogen atom in substituted benzoic acids is approximately proportional to the pK_a values expressed as Hammett σ constants. Ab initio molecular orbital calculations at the STO-3G level have shown that the nitrogen inversion barrier in substituted anilines[12] and the torsional barriers in para-substituted phenols,[13] respectively, parallel the extent of π charge transfer between the ring and the NH_2 and OH groups. Rotational barriers in mono-