Table I. Oxidation Quantum Yields of Tertiary Arylphosphines

Tertiary phosphine	Quantum yield[a]	Tertiary phosphine	Quantum yield[a]
PPh₃	3.3	PEtPh₂	3.6
PMePh₂	5.4	PEt₂Ph	4.5
PMe₂Ph	4.9		

[a] Measured in oxygen-saturated CH₂Cl₂ solution using 254-nm irradiation; values given are accurate to within ±10%.

simultaneously appear and increase at 1117 and 1188 cm⁻¹. The photoreaction can be induced with 254, 313, and 366 nm or with fluorescent room light irradiation. The 254-nm quantum yield of disappearance of PPh₃ is 3.3 ± 0.3. The mixed (alkyl–aryl)phosphines PMePh₂, PEtPh₂, PMe₂Ph, and PEt₂Ph are also photosensitive in the presence of oxygen and give uv and ir spectral changes similar to those obtained for PPh₃. The only product that we were able to isolate from irradiated PPh₃ solutions was Ph₃PO, and the lack of P–O–R vibrations in the infrared spectra of irradiated solutions of the other phenylphosphines suggests that the corresponding oxide is the major product in each case. Further, the ³¹P NMR spectra of irradiated CDCl₃ solutions of PPh₃, PMePh₂, PMe₂Ph, and PEtPh₂ each showed only a single resonance with chemical shifts of 30.1, 30.0, 33.7, and 34.3 ppm, respectively. These shifts are similar to those reported[8] for the corresponding oxides, and the ³¹P NMR spectrum of an authentic sample of MePh₂PO in CDCl₃ was identical with the spectrum of the irradiated PMePh₂ solution.

The 254-nm quantum yields for the phosphines studied (Table I) are all greater than 3 and imply that the oxidation proceeds through a free-radical chain mechanism. The photoactive excited state of the arylphosphines most likely results from the intense n → π* transition[9] centered around 260 nm, and various chain initiation pathways from this excitation can be proposed. A discussion of the detailed initiation and propagation mechanisms, however, must await further experimentation.

The high quantum yield oxidations reported herein and our previous findings[10,11] that many triphenylphosphine complexes are photosensitive only when irradiated in the presence of O₂ suggest that workers investigating the photochemical and thermal properties of tertiary phosphine complexes should seriously consider the possibility of photoinduced oxidation. It is especially important that kinetic and mechanistic studies of complexes that dissociate tertiary phosphines or studies employing an excess of tertiary phosphines be protected either from oxygen or from uv light. Ordinary fluorescent room light is of sufficient energy to induce the oxidation of the phosphines examined in this work.

Registry No. PPh₃, 603-35-0; PMePh₂, 1486-28-8; PMe₂Ph, 672-66-2; PEtPh₂, 607-01-2; PEt₂Ph, 1605-53-4.

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Charge Distribution and Carbon-13 Nuclear Magnetic Resonance Shifts in Tricarbonyl(dienyl)iron Cations

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Tricarbonyl(dienyl)iron cations in which the dienyl ligand possesses a "U" conformation are unusually stable.[2] This stability can be understood in terms of a frontier orbital model in which an occupied orbital on iron donates electrons to the nonbonding π LUMO of a dienyl cation (ψ_{NB}).[3,4] ¹³C NMR

ψ_{NB}
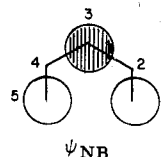
shifts show uncomplexed cyclohexadienyl(benzenium) cations are highly electron deficient only at carbons 1, 3, and 5,[5] as expected if ψ_{NB} is unoccupied. Electron donation to ψ_{NB} in iron-complexed cations ought to reduce or even reverse the charge alternation found in cyclohexadienyl cations.

¹³C NMR chemical shifts for three tricarbonyl(cyclohexadienyl)iron cations (e.g., **1**) have been published by Shubin


1
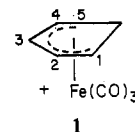
et al.[6] The relative importance of the several factors which determine NMR shifts of carbons bound to transition metals is not yet known.[7] Thus, application of the charge density–¹³C chemical shift correlation, which is well recognized for uncomplexed conjugated systems,[8] in the absence of independent evidence for its validity would be risky. Shubin et al. cautiously concluded that the Fe(CO)₃ group participates effectively in delocalization of the positive charge.

Recently, however, Hoffmann and Hofmann have calculated a charge distribution for cation **1** using the extended Hückel (E-H) method.[9] While the E-H atomic charges are quantitatively unreliable, the calculated charge distribution *pattern* should be valid. Carbons 1, 3, and 5 are predicted to be electron *rich* relative to carbons 2 and 4 with 1 and 5 bearing the largest net negative charges. There is a striking correlation between these results and the chemical shift data for **1**: C₁,₅ at 62.8 ppm, C₃ at 87.8 ppm, and C₂,₄ at 100.8 ppm.[10] The higher the calculated electron density is, the greater is the observed shielding.

The correlation between E-H charge density and ¹³C chemical shift is not unique to cyclohexadienyl ions. ¹³C NMR data for a series of acyclic cations **2–6** are presented in Table I.[11,12] The ¹J_{C–H} values for the dienyl carbons fall (within
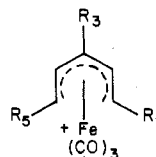
2, R₁ = CH₃, R₃ = R₅ = H
**3,** R₁ = R₅ = CH₃, R₃ = H
5, R₁ = R₃ = R₅ = CH₃
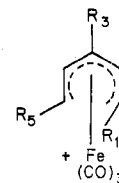
4, R₁ = R₅ = CH₃, R₃ = H
6, R₁ = R₃ = R₅ = CH₃

Table I. ^{13}C Chemical Shifts and Coupling Constants^a

Compd	$T,°C$	C_1	C_2	C_3	C_4	C_5	R_1	R_3	R_5	CO		
2	-57	91.0 (170)^b	103.2 (170)	95.3 (170)	103.7 (170)	62.0 (161)	20.4 (124)			206.7	197.7	
3^c	-57	87.5 (161)	103.2 (174)	90.9 (165)	103.2 (174)	87.5 (161)	20.5 (130)		20.5 (130)	208.1	198.6	
4^d	-51	77.5	99.0 (165)	97.5 (174)	104.7 (157)	81.9 (170)	15.6 (124)		20.6 (124)	208.2	198.4	198.1
5	-51	85.1 (165)	103.1 (165)	109.3	103.1 (165)	85.1 (165)	20.3 (128)	22.6 (130)	20.3 (128)	208.2	199.1	
6	-51,-62	74.5 (165)	96.5 (165)	117.6	104.3 (165)	80.2 (174)	16.0 (124)	23.3 (132)	20.7 (128)	208.3	198.7	198.4

^{a} Chemical shifts (±0.1 ppm) in ppm downfield from TMS; peaks measured relative to CDCl$_3$ (capillary) and converted using $\delta_{cap}{}^{CDCl_3} =$ 77.4 ppm. ^{b} $^1J_{C-H}$ (±5 Hz), measured from the coupled spectra, are given in parentheses. ^{c} Shifts recorded using the 1-deuterium derivative. ^{d} Shifts recorded using the derivative with 0.5 atom of deuterium in the 1 and 5 positions.

experimental error) within the range 165 ± 6 Hz, which is consistent with sp^2 hybridization. In ions 2 and 3, carbons 1, 3, and 5 are more highly shielded than carbons 2 and 4.[12] The same order of relative shielding is seen to persist in 5 after correction for the large deshielding of C$_3$ by an α methyl is made. We have computed E-H charge densities for the parent cation, 7.[13] The carbon atom charges shown exhibit the same

7
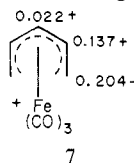
alternation pattern found for 1. The higher the calculated charge density is, the greater is the observed shielding: C$_{1,5}$ > C$_3$ > C$_{2,4}$. This close correlation lends credence to the idea that for the dienyl carbons of these ions, a group of carbons for which hybridization and molecular environment do not vary much, the carbon chemical shift is mainly a function of atomic charge.[14]

The syn, anti cations, 4 and 6 (after correction for the C$_3$-methyl), exhibit a similar shielding pattern, although the shifts of C$_2$ and C$_3$ are not very different. Thus, atomic charge is probably an important factor in determining these shifts as well. The shift differences $\delta_{C_1} - \delta_{C_5}$ and $\delta_{C_2} - \delta_{C_4}$ for these unsymmetrical ions are probably not primarily determined by charge differences. For example, the upfield shift of C$_5$ on going from 3 to 4 and from 5 to 6 arises from spatial proximity of C$_5$ and the anti methyl (R$_1$) in 4 and 6, analogous to the γ effect.[8] These shift differences may also reflect differences in Fe–C bonding.

Another significant feature of the NMR data is the presence at -50 °C of the maximum number of separate carbonyl carbon signals permitted by symmetry for each of the ions. These signals broaden and tend toward coalescence reversibly as the temperature is increased. For 6 three sharp peaks are observed at -51 °C. Warming to -30 °C causes broadening of all of the signals and coalescence of the two at higher field. At -18 °C two very broad peaks are observed. Slow site exchange for phosphite ligands has been observed for the closely related (dienyl)Fe(CO)$_{3-n}$(phosphite)$_n$ cations, with $n = 1$ or 2.[15]

^{13}C chemical shifts of carbons bound to transition metals have been interpreted in terms of atomic charges by a number of groups.[16] The magnitude of atomic charge effects observed in organic systems makes these interpretations seem reasonable, despite the lack of independent evidence for this choice from among the many factors that can affect the chemical shifts of such carbon atoms. Our results carry the strong implication that atomic charge does affect ^{13}C chemical shifts in tricarbonyl(dienyl)iron cations in a major way.

Experimental Section

^{13}C NMR spectra were obtained using a Bruker HX-90 spec-

trometer at 22.63 MHz with broad-band ^{1}H decoupling. The free-induction decay signal was accumulated and transformed using a Nicolet Series 1080 computer. Temperature was regulated by the Bruker BST-100/700 variable-temperature unit and calibrated using a copper–constantan thermocouple and potentiometer.

NMR samples were prepared using a modification of Brookhart's method.[17] A buffer layer of SO$_2$(l) was condensed on top of an FSO$_3$H–SO$_2$ mixture in an NMR tube and a tricarbonyl(dienol)iron complex was added as a CDCl$_3$ solution on top of the buffer layer.[18] The unmixed reagents were cooled at -50 to -78 °C and subsequently mixed with a glass rod. The CDCl$_3$ solution and the FSO$_3$H were degassed immediately prior to use, and all operations were carried out under nitrogen.

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(12) Solvent and counterion dependence of the shifts has been tested by examination of [2][BF$_4^-$] in SO$_2$ and nitromethane and [3][BF$_4^-$] in nitromethane. Although individual shifts exhibit solvent dependence, the shielding patterns discussed below are not changed.
(13) Calculations were charge iterative, and parameters used are the same as those employed by Hoffmann and Hofmann.[9] Calculations have also been carried out on cation 2 with similar results. Details on parameters and geometry used are available from the authors.
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