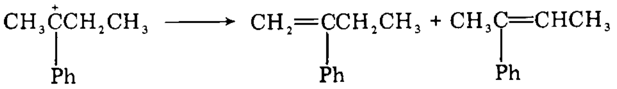
Table I. Selectivity and Reactivity of Tertiary Amines with Singlet *trans*-Stilbene

no.	amine	% a[a]	% b[a]	a/b,[b] cor	k_{rel}[b]
1	$CH_3\overset{a}{C}H_2N[\overset{b}{C}H(CH_3)_2]_2$	92	8	12 ± 1	1.0
2	$\overset{a}{C}H_3N[\overset{b}{C}H(CH_3)_2]_2$	>95	<5	>20 ± 2	0.92
3	$\overset{a}{C}H_3N(\overset{b}{C}H_2CH_3)_2$	63	37	2.3 ± 0.2	0.54
4	$(\overset{a}{C}H_3)_2N\overset{b}{C}H_2CH_3$	84	16	1.8 ± 0.2	
5	$(\overset{a}{C}H_3)_2N\overset{b}{C}H(CH_3)_2$	83	17	0.8 ± 0.1	0.97
6	$\overset{a}{C}H_3N(\overset{b}{C}D_3)$-*t*-Bu	69	31	2.2 ± 0.2	0.63

[a] Percent amine product determined by GC analysis for **1, 3, 4,** and **5** and by both NMR and MS isotope ratios for **6**. [b] See text.

amines. Reactivity increases with decreasing amine oxidation potential, in accord with an electron-transfer mechanism for singlet quenching.[3,6] Triisopropylamine and Dabco are more reactive quenchers of stilbene fluorescence than amine **1**, in accord with their lower oxidation potentials.[5] Thus the failure of these amines to form adducts must result from inefficient deprotonation of the aminium radical rather than inefficient aminium radical formation.

The results obtained for amines **3–5** are indicative of relatively nonselective deprotonation of the aminium radical by the stilbene radical anion. The small isotope effect for amine **6** is consistent with the small extent of bond breaking expected in a nonselective process. Deprotonation of aminium radicals is unlike the deprotonation of carbonium ions, the more substituted alkene generally predominating in E_1 reactions.[9] Cram and Sahyun observed that the yield of less-substituted alkene increases with increasing base strength. The low selectivity of amine **3–5** oxidation by stilbene may reflect the high basicity of the stilbene anion radical. Another example of nonselective



$$\mathrm{CH_3}\underset{\displaystyle \mathrm{Ph}}{\overset{+}{\mathrm{C}}}\mathrm{CH_2CH_3} \longrightarrow \mathrm{CH_2{=}}\underset{\displaystyle \mathrm{Ph}}{\mathrm{C}}\mathrm{CH_2CH_3} + \mathrm{CH_3}\underset{\displaystyle \mathrm{Ph}}{\mathrm{C}}\mathrm{{=}CHCH_3}$$

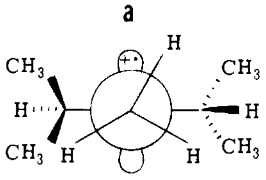
HOAc	26%	74%
N_2H_4	60%	40%

(5)

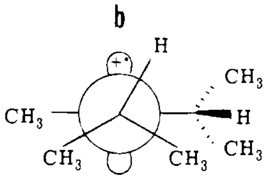
proton transfer from a radical cation (*p*-cymene) to a radical anion (trifluoroacetophenone) has recently been reported by Wagner and Puchalski.[8]

In contrast to the nonselective deprotonation of amines **3–5**, deprotonation of **1** and **2** is highly selective for formation of the less stable α-amino radical. Assuming that deprotonation requires at least partial overlap of the half vacant nitrogen p orbital with the developing carbon radical p orbital, the conformations of aminium radical **2** required for loss of type a and b protons are as shown. Steric interactions are clearly greater in b than in a. It is, in fact, impossible for a space-filling model

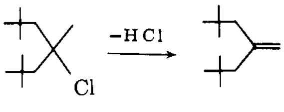
a



b



to attain conformation b. The situation is even worse for triisopropylamine, thus accounting for its lack of reactivity. The bicyclic structure of Dabco also prevents overlap of the nitrogen and α-carbon p orbitals.[11] We conclude that the selective oxidation of the tertiary amines **1** and **2** and the innertness of triisopropylamine are due to a stereoelectronic effect which is most evident when two or three of the alkyl groups are highly branched. We are aware of one apparently analogous E_1 reaction (eq 6) in which the less-substituted alkene is the sole product.[12]



(6)

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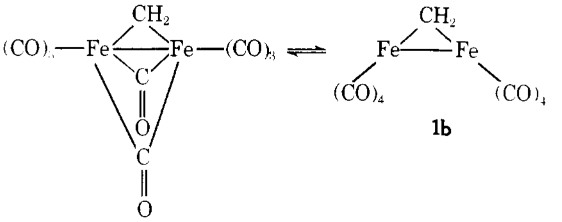
Synthesis, Crystal Structure, and Chemical Reactivity of Octacarbonyl-μ-methylene-diiron

Sir:

Complexes which possess a CH_2 group bridging two bonded transition metal atoms are of interest, inter alia, because of their relationship to methylene groups on metal surfaces in heterogeneous reactions. The electronic structure of such complexes has been studied theoretically.[1] We report the preparation, X-ray structural analysis, and chemical properties of the novel organometallic complex, $Fe_2(CO)_8CH_2$ (**1**), in which a CH_2 group bridges two iron atoms simultaneously linked by a metal-metal bond. Other complexes which possess a CH_2 group bridging two bonded transition metal atoms have recently been reported; e.g., Os–Os,[2] Ru–Ru,[3] Rh–Rh,[4] and Mn–Mn[5] containing species.



1a **1b**

Compound **1** is formed in 60% yield following reaction of the $[Fe_2(CO)_8]^{2-}$ ion with CH_2I_2 in acetone at 0 °C. The material crystallizes from ethyl acetate as air stable, golden

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Table I. Dependence of Crystallographic Least-Squares Refinement on Occupancy of Bridging Oxygen Atom Position

	room temperature		low temperature	
	$^2/_3$ occup O_{bridge}	full occup O_{bridge}	$^2/_3$ occup O_{bridge}	full occup O_{bridge}
	With Isotropic Thermal Parameters[a]			
R^b	0.118	0.126	0.102	0.110
$R_w{}^b$	0.136	0.145	0.120	0.132
$B_{iso}(O_{bridge})$, Å^2	4.4 (3)	8.0 (4)	3.6 (2)	6.4 (3)
$B_{iso}(O_{term})$, Å^2	5.0 (1)	4.9 (1)	4.0 (1)	4.0 (1)
	With Anisotropic Thermal Parameters			
R^b	0.029	0.046	0.028	0.045
$R_w{}^b$	0.033	0.060	0.034	0.064

[a] Numbers in parentheses are the estimated standard deviations in the least significant digit. [b] R and R_w are defined in ref 9.

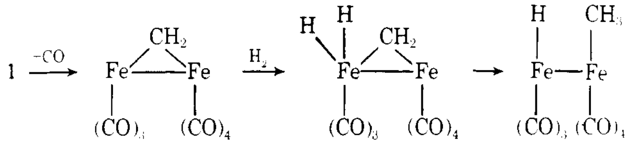
yellow, hexagonal prisms (mp 135 °C dec) which are very similar in appearance to the related carbonyl, $Fe_2(CO)_9$. The IR spectrum, taken as a mull in C_5Cl_6, displays bands at 2916 (w), 2072 (m), 2020 (s), 1875 (sh), and 1836 (s) cm^{-1}, the latter being indicative of bridging CO groups, as in **1a**; however, in CH_2Cl_2, benzene, or hexane solutions only terminal CO adsorptions are observed at 2112 (w), 2061 (s), 2031 (s), and 2016 (sh) cm^{-1}. The predominant structure in solution, then, is presumably **1b**; this behavior is also observed for the phenyl derivative of **1**[6] but not for the *p*-methoxyphenyl derivative,[7] which, from X-ray analysis, has a structure analogous to that of **1a**, and for which the IR spectrum is the same in solution and in the solid state.

The ^{1}H NMR spectrum of **1** displays a single absorption at δ 5.45 (acetone-d_6) and the Mössbauer spectrum[8] of the material shows both iron atoms to be equivalent, indicative of a bridging CH_2 group rather than an isomeric structure with a terminal carbene ligand. The mass spectrum exhibits peaks corresponding to the parent mass of **1** and to all fragments corresponding to the loss of CH_2 and/or CO ligands from **1**.

Crystals of **1** are hexagonal, space group $P6_3/m$ (No. 176), with unit cell constants at 22 °C of a = 6.502 (2) and c = 15.965 (12) Å.[9] Hence, the crystal structure of **1** is "isostructural" with that of $Fe_2(CO)_9$ (a = 6.436 and c = 16.123 Å)[10,11] and thus the molecule has C_{3h} ($\bar{6}$) symmetry imposed upon it. Consequently, the crystal structure of **1** is disordered, with the CH_2 group at a bridging position.[12] This description is supported by the refinement results for the structures[9] summarized in Table I. Isotropic least-squares refinements of both structures[9] converged with lower R indices and more reasonable thermal parameters for the bridging carbonyl oxygen atoms (vis-à-vis the terminal carbonyl oxygen atoms) when the number of bridging oxygen atoms was reduced from three to two per molecule, i.e., $^2/_3$ rather than unit occupancy for the crystallographically unique bridging oxygen atom. Furthermore, as shown in Table I, an even greater decrease in R index resulted when anisotropic refinement was carried out with this $^2/_3$ occupancy for the bridging carbonyl oxygen atom position.

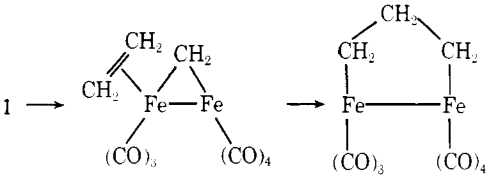
The structures of **1** at room temperature and low temperature[9] are identical and, with the exception of the Fe-Fe distance, in excellent agreement with the structure of $Fe_2(CO)_9$. In **1**, the Fe-Fe distance is 2.507 (1) Å, while in $Fe_2(CO)_9$ this distance is 2.523 (1) Å. At present, we can offer no satisfactory explanation for this difference. Owing to disorder,[12] the two types of bridging Fe-C distances cannot be distinguished.[13]

When compound **1** is treated with hydrogen (200 psi) at 60 °C in benzene, methane (81%) and small amounts of acetaldehyde (5%) are produced as well as $Fe_3(CO)_{12}$; similar reductions with mixtures of H_2 (200 psi) and CO (400 psi) yield the same organic products in approximately the same ratio but at a markedly decreased rate. (Here the inorganic product is $Fe(CO)_5$ rather than $Fe_3(CO)_{12}$.) This suggests that methane formation involves prior loss of a CO ligand from **1** to form **2**, which then undergoes oxidative addition of H_2 to give **3**, followed by intramolecular reductive elimination to the methyl complex **4**. Whether elimination of methane from **4** occurs directly, or whether the hydrogen atom migrates to the iron atom bearing the methyl group and then elimination occurs, is an interesting question, about which we have no evidence. Insertion of CO into the Fe-CH_3 bond of **4** followed again by reductive elimination would lead to acetaldehyde formation.

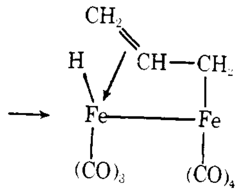


2 **3** **4**

Treatment of **1** at 55 °C in benzene with ethylene (400 psi) produces propylene (>90%) and $C_2H_4Fe(CO)_4$. Again, this reaction is inhibited by CO and is assumed to proceed via the olefin π complex **5**, followed by insertion of the olefin into the Fe-CH_2 bond, to generate the metallocycle **6**; β-hydride elimination by the coordinately unsaturated Fe atom of **6** to give the olefin π complex **7**, followed by reductive elimination, would lead to propylene. Consistent with this scheme is the fact that treatment of the $[Fe_2(CO)_8]^{2-}$ ion with 1,3-diiodopropane at 25 °C also generates propylene, presumably also via **6**.



5 **6**



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Similar treatment of **1** with propylene gives mainly isobutylene together with lesser amounts of *n*-butenes. With isobutylene there is no apparent reaction with **1**; however, an undetected reaction involving disproportionation of the CH_2 fragments between isobutylene and **1**, analogous to that reported by Parshall and co-workers for a Ti-CH_2-Al system,[14] has not yet been ruled out.

Another interesting reaction results when **1** is simultaneously treated with hydrogen and ethylene; in addition to the formation of both methane (66%) and propylene (6%)—the expected products from the two separate reactions discussed earlier—ethane (~600%) is obtained. The nature of the ethylene hydrogenation catalyst found in this reaction remains to be determined, but, under similar conditions, $C_2H_4Fe(CO)_4$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ are separately found to be ineffective catalysts for this hydrogenation.

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Supplementary Material Available: Table of fractional coordinates and anisotropic thermal parameters (1 page) for both crystallographic data sets. Ordering information is given on any current masthead page.

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(12) That is, each bridging position is occupied, statistically, $^2/_3$ by CO and $^1/_3$ by CH_2. Since the two presumably slightly different C positions would be indistinguishable by this experiment, the crystallographic description is thus one with a full-weight C (i.e., $^2/_3 + {}^1/_3$), a $^2/_3$-weight O ($^1/_3 + {}^1/_3$) and two $^1/_3$-weight H atoms at each bridging position.
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Ground-State Quenching of the ^2E Excited State of $Cr(bpy)_3{}^{3+}$ and $Cr(phen)_3{}^{3+}$ [1]

Sir:

The lowest metal-centered excited state (^2E) of polypyridyl complexes of Cr(III) [$Cr(NN)_3{}^{3+}$] has been shown to be a powerful oxidizing agent capable of engaging in excited-state electron-transfer reactions[2] and photoelectrochemical action.[3] Knowledge of the lifetime (τ) of ^2E is necessary in order to evaluate the photophysics of the state, calculate rate constants (k_q) from Stern-Volmer luminescence quenching, and engineer potential solar energy conversion schemes. Because of the thermal and photochemical stability of $Cr(NN)_3{}^{3+}$ in acidic aqueous solution,[2,4] 1 M HCl has been the medium of choice for many lifetime measurements. Examination of data from many laboratories[5-10] reveals variations in the values of τ and k_q for ostensibly identical systems and experimental conditions. We note, however, that the concentrations of the ground-state complexes are often not specified and can vary over many orders of magnitude depending upon the experimental technique or the application. In this communication we report the dependence of τ of (^2E)$Cr(phen)_3{}^{3+}$ (phen = 1,10-phenanthroline) and (^2E)$Cr(bpy)_3{}^{3+}$ (bpy = 2,2′-bipyridine) upon the concentration of the ground-state substrates.

Table I. Lifetime of (^2E)$Cr(phen)_3{}^{3+}$ in Deaerated Aqueous 1 M HCl Solutions at 22 °C

[$Cr(phen)_3{}^{3+}$], M	τ, ms[a]	[$Cr(phen)_3{}^{3+}$], M	τ, ms[a]
9.2×10^{-6}	0.36	2.7×10^{-4}	0.23
1.2×10^{-5}	0.34	5.6×10^{-4}	0.22
2.3×10^{-5}	0.37	6.7×10^{-4}	0.15
2.7×10^{-5}	0.33	1.2×10^{-3}	0.13
4.4×10^{-5}	0.36	2.0×10^{-3}	0.12
6.9×10^{-5}	0.29	5.0×10^{-3}	0.067
8.1×10^{-5}	0.30	7.5×10^{-3}	0.050
1.6×10^{-4}	0.31	1.0×10^{-2}	0.037
2.3×10^{-4}	0.22		

[a] Each value represents the average of three–ten individual runs.

Table II. Lifetime of (^2E)$Cr(bpy)_3{}^{3+}$ in Deaerated Aqueous 5 M HCl Solutions at 22 °C

[$Cr(bpy)_3{}^{3+}$], M	τ, ms[a]	[$Cr(bpy)_3{}^{3+}$], M	τ, ms[a]
1.2×10^{-5}	0.11	9.4×10^{-4}	0.084
2.8×10^{-5}	0.10	1.0×10^{-3}	0.078
4.6×10^{-5}	0.11	1.2×10^{-3}	0.081
4.7×10^{-5}	0.12	1.5×10^{-3}	0.082
5.7×10^{-5}	0.11	1.8×10^{-3}	0.077
9.4×10^{-5}	0.11	3.6×10^{-3}	0.060
1.0×10^{-4}	0.11	4.8×10^{-3}	0.073
2.0×10^{-4}	0.096	6.0×10^{-3}	0.047
2.8×10^{-4}	0.093	1.0×10^{-2}	0.041
4.7×10^{-4}	0.085	1.1×10^{-2}	0.044
6.0×10^{-4}	0.087	1.2×10^{-2}	0.042
9.0×10^{-4}	0.086		

[a] Each value represents the average of three–ten individual runs.

The complexes as $ClO_4{}^-$ salts were available from our previous studies.[2] Solutions were prepared from reagent grade (Fisher) HCl (10^{-5}% Fe and heavy metals) and water that had been distilled from $KMnO_4$ and/or purified by passage through a Millipore train; solutions were deaerated by bubbling with prepurified N_2 or Ar for 30 min. Values of τ were determined at 22 ± 1 °C by the monitoring of the first-order decay of the emission from ^2E at 727 nm excited by pulsed laser illumination. The apparatus in Montreal consisted of a 1-kW N_2 laser providing 4-ns pulses at 337 nm as previously described by Demas and Flynn.[11] The apparatus in Boston utilized a frequency-doubled ruby laser providing 30-ns pulses at 347 nm. The values of τ ($= 1/k_{obsd}$) within a single experimental set were reproducible with <10% variation; the standard deviation of values from replicate experiments were of the order of 10–15%.

The data for $Cr(phen)_3{}^{3+}$ in 1 M HCl given in Table I show that τ decreases by an order of magnitude as [$Cr(phen)_3{}^{3+}$] is increased from 1×10^{-5} to 1×10^{-2} M. The data produce a linear plot of k_{obsd} vs. [$Cr(phen)_3{}^{3+}$] (Figure 1) with a slope of 2.3×10^6 M^{-1} s^{-1} and an intercept of 3.0×10^3 s^{-1}. By comparison, the average of ten individual experiments yields $\tau = 0.25$ (± 0.03) ms over the substrate concentration range 1.2×10^{-5} to 1.2×10^{-3} M in the absence of HCl; solubility restrictions prevent the extension of the range in neat H_2O. The quenching phenomenon is the same in either 1 M HCl or 1 M NaCl. In contrast, τ values for (^2E)$Cr(bpy)_3{}^{3+}$ in 1 M HCl and neat H_2O are virtually indistinguishable: $\tau = 0.073$ (± 0.008) ms in 1 M HCl and 0.068 (± 0.008) ms in H_2O over the substrate concentration range 1.4×10^{-5} to 2.5×10^{-3} M. In order to observe the ground-state quenching phenomenon for $Cr(bpy)_3{}^{3+}$, 5 M HCl was used; the data (Table II) result in a linear quenching plot (Figure 2) with a slope of 1.3×10^6 M^{-1} s^{-1} and an intercept of 1.0×10^4 s^{-1}.

The use of different samples of the recrystallized complexes, analytical reagent grade acid, and purified water had no effect on the results. In order to exclude free ligand within the sub-

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