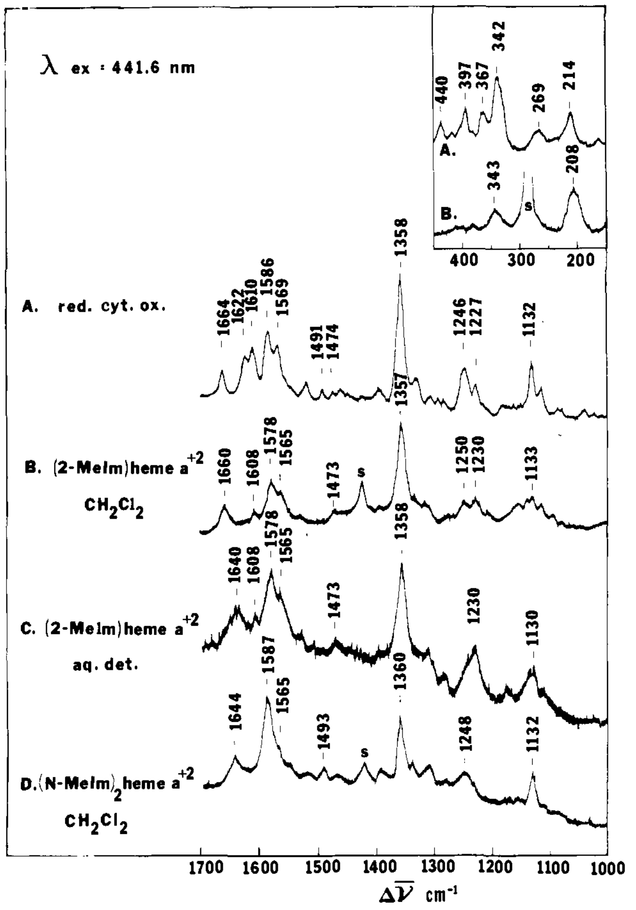

Figure 2. Resonance Raman spectra taken with 441.6-nm excitation, 15-mW incident power. Scan rate 50 cm^{-1} m^{-1}; time constant 1 s; spectral resolution 7 cm^{-1}. CH_2Cl_2 solvent peak marked "S". (A) Reduced cytochrome oxidase; (B) high-spin 2-methylimidazole heme a^{2+}/CH_2Cl_2; (C) high-spin 2-methylimidazole heme a^{2+}/aqueous CTAB; (D) low-spin bis(*N*-methylimidazole) heme a^{2+}/CH_2Cl_2. Heme concentrations: 60–120 μM. Inset: low-frequency region of traces A and B, reduced cytochrome oxidase and 2-methylimidazole heme a^{2+} dissolved in CH_2Cl_2, respectively.

The Raman spectra of the heme *a* model compounds, along with the spectrum of reduced oxidase, are shown in Figure 2. Soret laser excitation was used in the experiments, Franck-Condon scattering dominates, all modes in the spectra of Figure 2 have depolarization ratios $<{}^3/_4$.[14] Although the Raman spectrum of the reduced enzyme is composed of contributions from both cytochrome a^{2+} and $a_3{}^{2+}$, we showed in previous work[15] that some of the vibrations were due solely to cytochrome $a_3{}^{2+}$. These include the formyl vibration at 1664 cm^{-1}, the ring mode at 1230 cm^{-1}, and the low-frequency 214-cm^{-1} vibration. An investigation of the model spectra shows that for the high-spin ferrous heme *a* species in CH_2Cl_2 (Figure 2b) the formyl vibration occurs at 1660 cm^{-1} and reproduces the behavior of $a_3{}^{2+}$ well. In aqueous solution (Figure 2c) the high-spin heme *a* formyl vibration shifts to 1640 cm^{-1} which we interpret to reflect hydrogen bonding. In low-spin derivatives the carbonyl occurs at 1644 cm^{-1} in aprotic media (Figure 2d) and shifts to still lower frequency in protic solvents.[16] High-spin ferrous heme *a* in aprotic solvents also reproduces the $a_3{}^{2+}$ 1230-cm^{-1} mode. However, the frequency of this mode, in contrast to the formyl vibration, appears to be independent of solvent. In the low-frequency region (inset, Figure 2), five-coordinate high-spin ferrous heme *a* in CH_2Cl_2 shows a 208-cm^{-1} vibration which corresponds well with the $a_3{}^{2+}$ 214-cm^{-1} mode. This vibration is missing in the low-spin derivatives and weak or absent in high-spin species in protic solvents (not shown). By analogy with work on hemoglobin,[17] we had assigned the protein 214-cm^{-1} band to the $a_3{}^{2+}$ Fe–N_ϵ(histidine) vibration;[5a] the high-spin model compound provides additional support for this assignment. Moreover, a comparison of the $a_3{}^{2+}$ 214-cm^{-1} frequency with recent work by Stein et al.[18] indicates that in the protein the histidine N_δ is protonated and diminishes considerably the likelihood that this species serves as the bridging ligand between Cu_{a_3} and Fe_{a_3} in the dioxygen reducing site.[19]

The data on ferrous heme *a* model compounds solidify the assignment of cytochrome $a_3{}^{2+}$ as a five-coordinate, high-spin ferrous heme *a* species with an unaltered formyl in a non-hydrogen-bonding environment.[5a,20] That high-spin heme a^{2+} in CH_2Cl_2, but not in aqueous detergent solution, has optical properties in close agreement with $a_3{}^{2+}$, together with the IR data reported by Alben et al.,[5b] indicates that hydrophobic character in the dioxygen reducing site is not restricted to the immediate environment of the formyl group but rather is a property of a major portion of the pocket.

Acknowledgment. The portion of this research which was carried out at Michigan State University was supported by NIH Grant GM25480. We thank Patricia Callahan for helpful discussions.

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Correlation of Nonadditive Kinetic Effects with MINDO/3 Derived Molecular Geometries[1]

Jeffrey I. Seeman,* Roseanne Galzerano, and Keith Curtis

Philip Morris Research Center
Richmond, Virginia 23261

John C. Schug* and Jimmy W. Viers*

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

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Few studies have been reported which attempt to correlate chemical reactivity with molecular geometrical parameters.[2-6] A significant and valuable effort over the past 20 years has focused on the derivation of linear free energy relationships (LFER).[7] Although at least 11 different steric substitution parameters have

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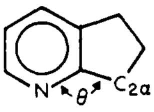
Table I. Alkylation Rate Constants and Basicity Properties of 1-13

compd	iodomethylation[a] 10^4k_2(exptl), L M^{-1} s^{-1}	k_{rel}	k_{calcd}[b]	10^3k_2 (CH_2=CH–CH_2Br),[c] L M^{-1} s^{-1}	pK_a[d]	ΔpK_a[f]	pK_a (calcd)[g]
pyridine (1)	3.18 ± 0.08	1		4.63	5.17[c]		
2-picoline (2)	1.38 ± 0.09	0.43		0.753	5.97[c]	0.80	
3-picoline (3)	5.40 ± 0.10	1.7		7.14	5.68[c]	0.51	
4-picoline (4)	6.76 ± 0.03	2.1		8.17	6.02[c]	0.85	
2,3-lutidine (5)	1.36 ± 0.07	0.43	0.73	0.734	6.60[c]		6.48
2,4-lutidine (6)	2.91 ± 0.06	0.92	0.90	1.46	6.72[c]		6.82
2,5-lutidine (7)	2.61 ± 0.01	0.82	0.73	1.24	6.47[c]		6.48
2,6-lutidine (8)	0.127 ± 0.003	0.040	0.18	~0.018	6.77[c]		6.77
3,4-lutidine (9)	10.7 ± 0.2	3.4	3.6	13.15	6.52[c]		6.53
3,5-lutidine (10)	8.28 ± 0.10	2.6	2.9	10.91	6.14[c]		6.19
2,3-cyclopentenopyridine (11)	6.14 ± 0.42	1.9	0.73		5.95[e]		
2,3-cyclohexenopyridine (12)	3.63 ± 0.04	1.1	0.73		6.65[e]		
2,3-cycloheptenopyridine (13)	0.965 ± 0.018	0.30	0.73				

[a] At 25.00 ± 0.01 °C in acetonitrile. These data represent an average of four alkylations per compound. [b] Calculated assuming LFER, e.g., k_{calcd} for 3,4-dimethylpyridine = k_{rel}(3-methylpyridine) × k_{rel}(4-methylpyridine). [c] Reference 11c. [d] For additional pK_a literature values, see ref 8j and 11a. [e] Determined in HOAC/Ac_2O by: Thummel, R. P.; Kohli, D. K. *J. Org. Chem.* 1977, *42*, 2742-2747. [f] $\Delta pK_a(i) = pK_a(i) - pK_a(1)$ [g] $pK_a(\text{calcd}) = pK_a(1) + \sum_i \Delta pK_a$ where *i* incorporates all substituents in each case.

been proposed,[8] structural consequences of these substituents are not evaluated per se by LFER treatments. Nonadditive substituent effects are an important and complex subset of structure–reactivity considerations.

DeTar recently suggested that doubts regarding the validity of steric LFER's must be met by theoretical and experimental investigations of systems which exhibit nonadditive effects.[2] In this work, we examine the postulate that theoretically derived ground-state geometries can be directly related to transition-state effects for a series of compounds. We have employed MINDO/3 semiempirical all-valence electron calculations to determine ground-state equilibrium geometries for a series of pyridine derivatives **1–13** (Table I) and have examined the iodomethylation of these compounds. We now report an excellent correlation of molecular geometrical parameters with chemical reactivity for this series of compounds which demonstrate nonadditive kinetic effects.



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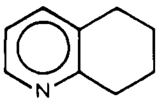

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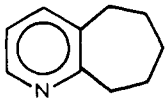

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The iodomethylation reactions were run in acetonitrile at 25 °C, and the rates were determined by using conductometric methods reported previously.[9] While the iodomethylation of pyridine and many of its methylated derivatives have been examined in the past,[10] there is no report, to our knowledge, which has studied the iodomethylation of all the picolines and lutidines under the same reaction conditions. The reaction rate constants $k_{2(\text{exptl})}$ and the relative reaction rate constants k_{rel} are listed in Table I. Substituent effect additivity can be tested by using the picoline relative rates as standards. Thus, the values of k_{calcd} in Table I were obtained by using multiplicative contributions of 0.43, 1.7, and 2.1, respectively, for each 2-, 3-, and/or 4-alkyl substituent. Reasonably good agreement is found between the calculated and experimental rate constants, except for 2,6-lutidine and the 2,3-disubstituted pyridines. Nonadditivity is observed as evidenced by noting that **11** iodomethylates 6.3 times faster than **13**.

Table II. Steric Accessibility Factor and Geometric Parameters[a] of 2-Substituted Pyridines

compd	S[b]	d_{NH},[a,c] Å	θ,[b,d] deg
2-picoline (2)	1	2.596	117.01
2,3-lutidine (5)	0.59	2.537	114.23
2,4-lutidine (6)	1.0	2.595	117.07
2,5-lutidine (7)	1.1	2.601	117.36
2,3-cyclopentenopyridine (11)	2.6	2.924	127.12
2,3-cyclohexenopyridine (12)	1.5	2.688	117.44
2,3-cycloheptenopyridine (13)	0.41	2.473	114.12

[a] Geometries obtained via complete MINDO/3 energy minimization calculations. [b] $S \equiv k_{rel}/k_{calcd}$; see Table I for rate data. [c] Distance from pyridine nitrogen to closest hydrogen on $C_{2\alpha}$. [d] N–C_2–$C_{2\alpha}$ angle.

For comparative purposes, the pK_a's for most of these compounds are also listed in Table I. While the pK_a's exhibit much better additivity properties than do the relative rate constants, they do not correlate well with either $k_{2(\text{exptl})}$ or ln $k_{2(\text{exptl})}$. Since excellent correlations have been obtained between alkylation rates and pK_a's for series of 2-heterosubstituted pyridines,[10b,d,11] we conclude that the iodomethylation effects reported herein are not primarily electronic in nature. However, it was first necessary to eliminate the possibility of unusual solvent effects in these reactions. One criterion would be the establishment of identical relative rates of alkylation in a different solvent.[2,12] Clark and Rothwell[11c] have previously examined the allylbrominations of **1–10** in nitrobenzene at 60 °C; a comparison of their allylbromination data with the iodomethylation rate constants found

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in this work reveals a remarkably significant correlation ($r = 0.981$, $p < 0.001$), suggesting that differential solvation within this series is unimportant.

A quantitative measure of the nonadditivity can be obtained for the alkylation reaction by defining $S = k_{rel}/k_{calcd}$ for each α-substituted compound (Table II). The definition of S leads to a value of $S = 1$ for 2-picoline, consistent with DeTar's recent criterion for a sterically unstrained standard.[13] A value of $S > 1$ implies less steric hindrance relative to 2-picoline, and $S < 1$ indicates the converse.

To relate S to structural properties, we performed complete geometry optimizations by using the MINDO/3 program of Rinaldi[14,15] for **1**-**13**. The bond lengths and angles calculated for pyridine compare very favorably with those determined by microwave spectroscopy and electron diffraction studies.[16] Experimental information relevant to the structure of **2**-**13** is rare,[17] but some data exist for their benzene analogues.[18] We have therefore performed complete MINDO/3 energy minimization for benzene, toluene, the xylenes *o*-di-tert-butylbenzene, indane, and tetralin.[19] Comparison of the available experimental data[18] for these nonheterocyclic aromatic compounds with the semiempirical results indicates that the MINDO/3 method does predict appropriate trends in the bond angles and lengths calculated.

For the 2-substituted pyridines, the key geometric parameters appear to be θ, the $N-C_2-C_{2\alpha}$ bond angle, and d_{NH}, the distance from nitrogen to the closest hydrogen on the α carbon (see Table II). A wide range in both θ and d_{NH} is found, spanning 13.00° and 0.451 Å, respectively. 2,3-Lutidine (**5**) iodomethylates with one-half the rate of 2,5-lutidine. That **5** fails to satisfy a LFER due to a buttressing effect is seen in Table II as a 3.13° *decrease* in θ and a 0.064 Å *decrease* in d_{NH} relative to 2,5-lutidine. At the other extreme, tying the methyl groups together with a methylene unit in 2,3-cyclopentenopyridine (**11**) *increases* both θ (by 10.29°) and d_{NH} (by 0.334 Å) relative to 2,5-lutidine; **11** iodomethylates almost five times faster than does **5**.

Excellent correlations are found for the nonadditivity factor S as a function of both θ ($S = -17.700 + 0.160\theta$; $r = 0.970$, $p = 0.001$) and d_{NH} ($S = -11.844 + 4.950d_{NH}$; $r = 0.996$, $p < 0.001$). The parameters θ and d_{NH} are highly correlated with one another ($r = 0.971$, $p = 0.001$) and are not independent.

That θ (and d_{NH}) so strongly correlate with the observed kinetics is a unique demonstration of the relationship between substrate equilibrium geometry and reaction rate. The coupling of chemical kinetics with theoretical treatments for compounds which fail to follow LFER will lead to a better understanding of non-additive substituent effects.

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(19) Complete details will be reported in the full paper.

Formation of an Iridium Ethyl Complex by Methyl Migration to a Coordinated Methylene Group

D. L. Thorn* and T. H. Tulip

Contribution No. 2907
Central Research and Development Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

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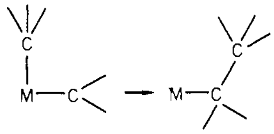
Despite the importance of migratory reactions in organometallic chemistry,[1] examples of one potentially useful class of migrations—alkyl migration from a metal atom to the carbon atom of a coordinated carbene or alkylidene ligand (equation 1)—have only recently been encountered.[2-5] While a large number of alkylalkylidene complexes of the earlier transition metals are known, they apparently show no tendency to undergo this reaction, owing to the pronounced nucleophilicity of the alkylidene carbon atom.[6] In contrast, electrophilic carbene complexes of the later transition metals often readily react with external nucleophilic reagents,[7-9] and it is in such complexes that the reaction illustrated in equation 1 is most likely to be facile. In this communication we report the synthesis and characterization of a compound with an alkyl group cis to an electrophilic carbene precursor ligand, the iridium methyl(methoxymethyl) complex $IrBr(CH_3)(CH_2OCH_3)(P(CH_3)_3)_3$ (**1**). Compound **1** is readily transformed into a transient methylmethylene complex, which subsequently undergoes methyl migration to the methylene group. A stable ethyl complex has been isolated, and its structure has been confirmed by a single-crystal X-ray diffraction study.



(1)

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