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- (14) (a) NMR spectra were recorded in CDCl<sub>3</sub> and IR spectra in toluene.  $\sigma$  is reported as parts per million downfield from internal HMDS for <sup>1</sup>H and Me<sub>4</sub>Si for <sup>13</sup>C except where noted. Complex:  $\nu_{CO}$  (cm<sup>-1</sup>);  $\delta$  (multiplicity, relative intensity) with s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. **2a**: (1928) [<sup>1</sup>H] CH<sub>3</sub> 3.09 (s, 3 H), 3.15 (s, 3 H), 3.17 (s, 3 H), 3.30 (s, 3 H). **2b**: (1925) [<sup>1</sup>H] CH<sub>3</sub> 1.10–1.39 (m, 12 H); CH<sub>2</sub> 3.49–3.82 (m, 8 H); [<sup>13</sup>C] (room temperature) CH<sub>3</sub> 12.30, 12.43, 12.84; CH<sub>2</sub> 44.18, 44.52, 45.99;  $\equiv$ CH 206.7; (–50 °C) C<sub>dtc</sub> 198.9, 211.7;  $\equiv$ CH 206.1, 207.3; CO 237.3. **3a**: (1914) [<sup>1</sup>H] CH<sub>3</sub> of dmct and  $\equiv$ CCH<sub>3</sub> 3.08–3.38 (m). **3b**: (1910) [<sup>1</sup>H] (CD<sub>2</sub>Cl<sub>2</sub>) CH<sub>3</sub> 1.00–1.40 (m, 12 H); CH<sub>2</sub> 3.4–3.8 (m, 8 H);  $\equiv$ CCH<sub>3</sub> 3.18 (s, 6 H). **4a**: (1911) [<sup>1</sup>H] CH<sub>3</sub>(hexyne) 1.22 (t, 6 H); CH<sub>3</sub>(dtc) 3.09 (s, 3 H), 3.16 (s, 3 H), 3.17 (s, 3 H), 3.29 (s, 3 H); CH<sub>2</sub>(hexyne) 3.76 (q, 4 H). **4b**: (1910) [<sup>1</sup>H] CH<sub>3</sub> (hexyne and dtc) 1.04–1.30 (m, 18 H); CH<sub>2</sub> (hexyne and dtc) 3.48–3.88 (m, 12 H). **5a**: (1928) [<sup>1</sup>H] CH<sub>3</sub> 3.15 (s, 3 H), 3.16 (s, 3 H), 3.20 (s, 3 H), 3.24 (s, 3 H); Ph 7.14–7.70 (m, 10 H). **5b**: (1927) [<sup>1</sup>H] CH<sub>3</sub> 1.07–1.36 (m, 12 H); CH<sub>2</sub> 3.44–3.80 (m, 8 H); Ph 7.20–7.66 (m, 10 H). **6a**: (1925) [<sup>1</sup>H] CH<sub>3</sub> 3.10 (s, 3 H), 3.12 (s, 3 H), 3.18 (s, 3 H), 3.24 (s, 3 H);  $\equiv$ CPh 7.32–7.93 (m, 5 H);  $\equiv$ CH 13.48 (s, 1 H), (–70 °C) 13.66 (s, 1 H). **6b**: (1924) [<sup>1</sup>H] CH<sub>3</sub> 1.04–1.33 (m, 12 H); CH<sub>2</sub> 3.43–3.88 (m, 8 H);  $\equiv$ CPh 7.24–7.99 (m, 5 H),  $\equiv$ CH 13.34 (s, 1 H) (–60 °C) 13.60 (s, 1 H); [<sup>13</sup>C] CH<sub>3</sub> 12.2, 12.4, 12.8; CH<sub>2</sub> 43.9, 44.1, 44.5, 45.8; Ph(ortho) 128.5, (meta) 131.8, (para) 129.3, (ipso) 136.4; C(dtc and  $\equiv$ CPh, unassigned) 199.9, 210.9, 213.1;  $\equiv$ CH 205.7; CO 237.9. **7a**: (1937) [<sup>1</sup>H] CH<sub>3</sub> 2.98 (s, 3 H), 3.08 (s, 3 H), 3.13 (s, 3 H), 3.14 (s, 3 H); Ph 6.96–7.60 (m, 10 H). **7b**: (1935) [<sup>1</sup>H] CH<sub>3</sub> 1.12 (q, 12 H); CH<sub>2</sub> 3.20–3.68 (m, 8 H); Ph 6.80–7.50 (m, 10 H). (b) Pertinent coupling constants for **2b** in hertz at room temperature unless otherwise noted. **2b**: <sup>1</sup>J(W–C<sub>CO</sub>) = 144; <sup>2</sup>J(C<sub>CO</sub>W–C<sub>CO</sub>) = 22; <sup>3</sup>J(C<sub>CO</sub>WCH) = 3; (–95 °C) <sup>3</sup>J(C<sub>CO</sub>WCH<sub>a</sub>) = ±7; <sup>3</sup>J(C<sub>CO</sub>WCH<sub>b</sub>) = ±1; <sup>1</sup>J(C<sub>CO</sub>≡CH) = 210; <sup>2</sup>J(C<sub>CO</sub>≡CH) = 7.
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## Resonance Energies of $\pi$ -Hydrocarbon-Iron Tricarbonyl Complexes<sup>1</sup>

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**Abstract:** Tricarbonyl(tetrahapto-unsaturated hydrocarbon)iron complexes are described as resonance hybrids of valence-bond structures. Quantitative structure-resonance theory and previously established graph-theoretical algorithms are used to describe the complexes and to calculate resonance energies. The results are in agreement with experimental properties of these complexes.

Resonance energies,<sup>2,3</sup> bond orders,<sup>4,5</sup> heats of formation,<sup>6-8</sup> ionization potentials,<sup>9</sup> and reactivity indexes<sup>10-13</sup> for hydrocarbon  $\pi$  systems can be obtained using an empirical valence bond theory with a highly limited basis of Kekule structures. This theoretical framework is termed structure-resonance theory, and its applications have been recently reviewed.<sup>14</sup> The numerical results correlate precisely with experimental properties and with the results of LCAO-MO-SCF calculations. Graph-theoretical algorithms for counting structures<sup>15,16</sup> and an accurate empirical logarithmic relationship<sup>17</sup> between structure count (SC) and resonance energy (RE) allow the theory to be applied rapidly.

The same formalism can be used to describe transition-metal complexes with  $\pi$  hydrocarbon ligands. This paper summarizes resonance energies for tricarbonyl(tetrahapto-unsaturated hydrocarbon)iron derivatives obtained by this approach. The



















results allow one to quantitatively rationalize relative stabilities and fluxional behaviors of iron complexes of this type.

**Valence Model.** A topological, Hückel-type, orbital model is used that has been previously employed by Mingos<sup>18</sup> to discuss the bonding in metal  $\eta^3$ - and  $\eta^4$ -unsaturated hydrocarbon complexes. In this model, the complex is described as a metal-hydrocarbon fragment perturbed to a negligible extent by the carbonyl groups. Justifications derive from experimental studies of photoelectron spectra,<sup>19,20</sup> ab initio calculations,<sup>19,21</sup> semiempirical MO calculations,<sup>22,23</sup> and perturbation theory arguments.<sup>24</sup>

The basic set for tricarbonyl(butadiene)iron and graphs of the bonding network are depicted in **1**. Iron hybrid  $d_{x^2-y^2}$  and  $d_{yz}$ - $p_y$  orbitals are assumed to combine with the organic ligand p orbitals to form a three-dimensional delocalized electronic network containing  $n/2$  electrons, where  $n$  is the total number



Table I. Resonance Energies of Tricarbonyliron Complexes









organic $\pi$ ligand <sup>a</sup>	ligand RE, eV <sup>b</sup>	complex			$\Delta$ RE, eV	complex status <sup>e</sup>
		SC	CSC	RE, eV <sup>c</sup>		
	-0.65	4	4	1.80	2.45	A
	-1.06	3	3	1.43	2.49	A
	-0.05	5	5	2.09	2.14	A
	0.0	4	4	1.80	1.80	A
	0.0	4	4	1.80	1.80	B
	0.0	5	3	1.43	1.43	B
	0.0	3	3	1.43	1.43	A
	-0.33	4	2	0.90	1.23	C
	1.35	7	7	2.53	1.18	A
	1.60	10	8	2.70	1.10	A
	0.81	4	4	1.80	0.99	B
	0.47	3	3	1.43	0.96	A
	1.35	7	5	2.09	0.74	C
	0.88	4	2	0.90	0.02	C
	0.0	10	8	2.70	2.70	A
	0.0 <sup>d</sup>	10	8	2.70	2.70	A
	0.81	10	10	2.99	2.18	A
	0.81	10	8	2.70	1.89	C

<sup>a</sup> The site of tricarbonyliron attachment is indicated by heavy lines.  
<sup>b</sup> Reference 3, 17, and 36. <sup>c</sup> RE (complex) = 1.30 ln CSC. <sup>d</sup> Assumption. <sup>e</sup> Reference 37. A = known compound, B = simple derivative known, C = unknown.

observed order of activation energies. However, quantitative estimates of the activation energies can also be made, assuming the previously used relationship, RE = 1.30 ln CSC, and assuming that the base value of 8.1 kcal for the cyclooctatetraene isomerization<sup>46</sup> can be carried over into each reaction. The agreement with experiment is reasonable, especially considering the simplicity of the calculations. It should be mentioned that the activation energy for the degenerate rearrangement of tricarbonyl( $\eta^4$ -cycloheptatriene)iron,  $\Delta G^\ddagger = 22.3$  kcal,<sup>47,48</sup> cannot be rationalized in terms of a 1,2-shift mechanism, calculated  $\Delta E^\ddagger = 41$  kcal. A complexed noncaradiene intermediate has been proposed,<sup>47,48</sup> and consequently this reaction should not fit the pattern of those outlined in Table II.

The postulate that delocalization and resonance energy increase upon complexation, and the correlation of this increase with stability, is a fundamental difference between this work and conventional molecular orbital treatments of the complexation phenomena. Previously the complexing reaction was

Table II. Fluxional Tricarbonyliron Complexes

SC (reactant)	SC (intermediate)	$\Delta E^\ddagger$ , kcal (exptl)	$\Delta E^\ddagger$ , kcal (calcd)
4 	4 	8.1 <sup>a</sup>	(8.1)
7 	5 	18.6 <sup>b</sup>	18.2
10 	6 	23.6 <sup>c</sup>	23.4
3 	1 	33 <sup>d</sup>	41.0

<sup>a</sup> Reference 46. <sup>b</sup> Reference 44. <sup>c</sup> Recalculated from data given in ref 44. <sup>d</sup> Estimate based on rate constants given in ref 42 assuming Arrhenius  $A$  factor =  $10^{13.5}$ .

thought to give a loss of resonance energy,<sup>38,49</sup> and sites of lowest localization energy were considered to be preferred sites of reaction.<sup>18,41,50</sup> However, the concepts of "three-dimensional aromaticity"<sup>51</sup> and "metalloaromaticity"<sup>21</sup> recently defined for complexes of the type considered here are in agreement with the idea of substantial resonance stabilization in these compounds. One distinguishing advantage of the structure-resonance approach is that a calculation can be carried out by hand in a few seconds, allowing numerous applications with little labor.

The NBMO coefficients in 4 allow the calculation of other quantities of interest, i.e., bond orders and localization energies of various types.<sup>14</sup> These applications, extensions to other metal-organic systems, and the relationship of this approach to earlier valence-bond descriptions of metal-organic complexes<sup>52,53</sup> are under investigation.

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- Assuming an equally weighted hybrid of structures, the resonance energy

is calculated from the equation  $RE = (2 + SC) \sum H_{ij}$ , where SC is the structure count and the  $H_{ij}$  are resonance integrals that correspond to energies for permutations of pairs of electrons over the bonding network. Additional integrals needed for other calculations are  $\gamma_2 = 0.34$  eV (conjugated circuit of ten orbitals) and  $\omega_2 = -0.26$  eV (conjugated circuit of eight orbitals).

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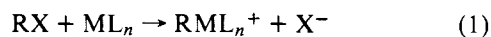
## Relative Reactivities of Methyl Iodide and Methyl Tosylate with Transition-Metal Nucleophiles<sup>1</sup>

Ralph G. Pearson\*<sup>2</sup> and Phillip E. Figdore<sup>3</sup>

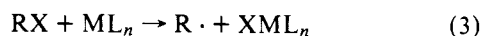
Contribution from the Chemical Laboratories, Northwestern University, Evanston, Illinois 60201, and the University of California at Santa Barbara, Santa Barbara, California 93106. Received June 13, 1979

**Abstract:** The rate constants  $k_1$  and  $k_{OTs}$  are determined for the reaction of methyl iodide and methyl tosylate with a number of transition-metal nucleophiles. The values of  $k_1$  cover a span of  $10^{11}$  in magnitude. The ratio  $k_1/k_{OTs}$  covers a range from  $10^9$  to  $10^{-3}$ , with some nucleophiles not reacting with methyl tosylate before undergoing decomposition. Unfortunately, except for  $Co(CN)_5^{3-}$ , the ratio cannot be used as a guide to free-radical mechanisms. Except for  $Li_2Cu_2Me_4$ ,  $Li_2AuMe_2$ , and  $Li_2PtMe_4$ ,  $\log k_1$  plotted against  $\log k_{OTs}$  gives a straight line, suggesting a common  $S_N2$  mechanism. The permethylated complexes are unique in having  $k_1/k_{OTs}$  less than unity.

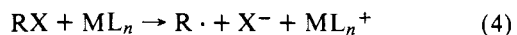
The reactions of transition-metal complexes,  $ML_n$ , with alkyl halides and with alkyl sulfonates are of great importance both in the synthesis of organometallic compounds and, by subsequent reactions, in organic synthesis. In these reactions the transition-metal complex acts as a nucleophilic reagent. It can also be regarded as the substrate in a typical oxidative-addition reaction, whether or not both R and X are added to the metal.



Oxidative additions of alkyl halide have been found to occur by a variety of mechanisms.<sup>4</sup> Simple  $S_N2$  substitution mechanisms are most common, followed by free-radical pathways, next most common. In a few cases concerted addition of RX has been shown to occur.<sup>5</sup> Two kinds of free-radical paths have been postulated: (a) initiation by attack of the metal atom on the halogen of  $RX^6$



(b) initiation by electron transfer from  $ML_n^7$

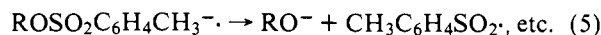


Since the products, and their stereochemistry, often depend critically upon the reaction mechanism, it is important to be able to anticipate which reaction path is likely to be found for a given RX and  $ML_n$ . Previous work allows some generalizations to be made.<sup>8</sup> Free-radical mechanisms become more likely as R varies, primary < secondary < tertiary < benzyl

or allyl. Also free-radical mechanisms are more likely as X changes,  $RSO_3^- < Cl^- < Br^- < I^-$ .

These observations are useful as far as RX is concerned. However, there is no clear-cut pattern for the role of the metal atom, or its ligands, in predicting the behavior of a given  $ML_n$ . In the  $S_N2$  mechanism the metal changes its oxidation state by two units. In the free-radical mechanisms, intermediates or, in some cases, products are formed in which the metal atom changes its oxidation state by only one unit. In some cases this can be a useful guide for prediction. However, transition metals have a variety of oxidation states possible, including unstable ones in the case of intermediates. This makes predictions much more hazardous.

As mentioned above, alkyl sulfonates, such as ROTs, seem reluctant to react by free-radical paths. Powerful electron donors, such as sodium naphthalene, will transfer an electron to an alkyl tosylate.<sup>9</sup> The products that are formed result from cleavage of the sulfur-oxygen bond.



Such products are not observed in reactions of transition-metal complexes with alkyl sulfonates.

The supposition that alkyl tosylates, or sulfonates, will not react by a free-radical path has been critically tested for one case. The complex  $Co(CN)_5^{3-}$  is known to react by halogen abstraction as shown in eq 3.<sup>6a,8a</sup> The molecules  $CH_3O-SO_2C_6H_5$ ,  $CH_3OSO_2C_6H_4CH_3$ , and  $CH_3CH(OTs)CO_2C_2H_5$  were found not to react with  $Co(CN)_5^{3-}$  in 24 h.<sup>10</sup> The corresponding iodides reacted readily and a ratio of  $k_1/k_{OTs} > 10^9$  was indicated.