

Figure 2. The dependence of $1/\Phi_D$ on the concentration of ethyl iodide.

as $k'_{isc}[Q]$ becomes very large. If $\Phi_{isc} \cong 1$, then one will obtain

$$\frac{1}{\Phi_D} = \frac{k_2[A] + k_q[A] + k_d}{k_2[A]} + \frac{k'_q[Q]}{k_2[A]}$$

which indicates that $1/\Phi_D$ should be a linear function of $[Q]$, the heavy-atom solvent concentration.

The data in Table I indicate that as the concentration

Table I. Solvent Dependence of Product Distribution for Dimerization of Acenaphthylene

| Mol % EtI ^a | % cis | % trans |
|------------------------|-------|---------|
| 0 | 56 | 44 |
| 5 | 19 | 81 |
| 10 | 18 | 82 |
| 15 | 22 | 78 |
| 20 | 21 | 79 |
| 25 | 23 | 77 |
| 30 | 29 | 71 |
| 40 | 28 | 72 |
| 50 | 24 | 76 |
| 60 | 27 | 73 |
| 75 | 30 | 70 |
| 90 | 29 | 71 |
| 100 | 32 | 68 |

^a Cyclohexane was used as a cosolvent in all samples containing less than 100 mol % EtI.

of ethyl iodide increases, there is a moderate increase in the proportion of cis dimer that is formed.¹⁰ This is in agreement with the findings of Hartmann, Hartmann,

(10) (a) Solutions of pure cis and pure trans dimers in cyclohexane were prepared and the molar absorptivities at 314 and 284 nm for each were determined: cis $\epsilon_{314} 1.78 \times 10^4$, $\epsilon_{284} 1.02 \times 10^4$; trans $\epsilon_{314} 3.93 \times 10^3$, $\epsilon_{284} 1.18 \times 10^4$. The composition of the product dimer mixtures was determined by measuring the optical densities of cyclohexane solutions of these dimers at 314 and 284 nm. From these optical densities and the corresponding molar absorptivities, the concentrations of the cis and trans dimers were calculated. (b) The dimer mixtures were prepared for analysis in the following manner. Each irradiated solution was transferred to a sublimator cavity, taken to dryness, and sublimed at 50° to remove unreacted acenaphthylene. The residue was then dissolved in enough cyclohexane to yield a $\sim 5 \times 10^{-5}$ M solution for uv analysis.

and Schenck who observed that the percentage of triplet-derived cis dimer increased as the polarity of the solvent system increased.¹¹ This is the result of increased stabilization of the transition state leading to the cis dimer relative to that leading to the trans.^{7,11,12}

The results cited above indicate that there is a practical limit to the amount of heavy-atom solvent enhancement one can obtain for a given photochemical reaction. Attempts to exceed this limit may in fact lower the quantum yield of the desired product. Work is in progress to determine many of the above rate constants as well as to elucidate the mechanism of both external and internal heavy-atom perturbation.

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(11) I. M. Hartmann, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **100**, 3146 (1967).

(12) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).

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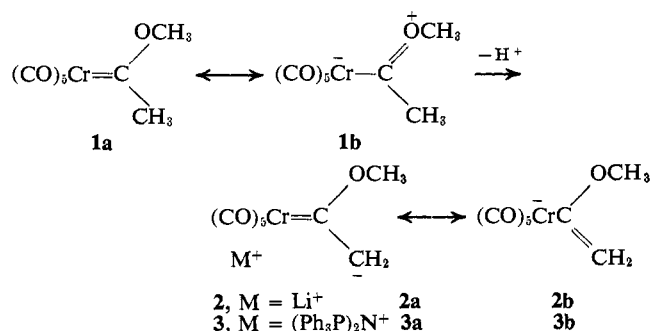
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Structure and Basicity of Anions Generated α to the Carbene Carbon Atom of Transition Metal-Carbene Complexes

Sir:

The kinetic acidity of protons attached to the carbon atom α to the carbene carbon atom of transition metal-carbene complexes^{1,2} implies the existence of an intermediate anion. Recently we reported the stoichiometric generation of such "carbene anions" (2) and their



behavior as carbon nucleophiles in reactions with DCl, methyl fluorosulfonate, benzaldehyde, and acetyl chloride.^{3,4} Here we report the isolation of a stable bis-(triphenylphosphine)iminium salt of 3, the spectroscopic characterization of 3 as a vinyl chromium anion, and the remarkably high thermodynamic acidity of the transition metal-carbene complex 1.

Quantitative generation of the lithium salt of the carbene anion (2) was achieved by addition of 1 equiv of *n*-butyllithium to a solution of (methylmethoxycarbene)pentacarbonylchromium(0) (1) in tetrahydrofuran

(1) C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, **7**, 390 (1968).

(2) The kinetic acidity of metal-carbene complexes has been used in structural elucidation studies of transition metal-carbene complexes: C. P. Casey, *Chem. Commun.*, 1220 (1970).

(3) C. P. Casey, R. A. Boggs, and R. L. Anderson, *J. Amer. Chem. Soc.*, **94**, 8947 (1972).

(4) C. P. Casey, R. A. Boggs, D. F. Marten, and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 243 (1973).

Table I. Infrared Spectra of Substituted Pentacarbonylchromium Compounds

| | Ref | Solvent | Carbonyl stretching frequencies (cm ⁻¹) |
|--|----------|---------|---|
| (CO) ₅ Cr=C(OCH ₃)CH ₃ (1) | | THF | 2062 (m), 1980 (s), 1941 (vs) |
| [(CO) ₅ CrC(OCH ₃)CH ₂] ⁻ [(Ph ₃ P) ₂ N] ⁺ (3) | | THF | 2030 (w), 1937 (w), 1898 (vs), 1849 (s) |
| [(CO) ₅ CrC(OCH ₃)CH ₂] ⁻ Li ⁺ | | THF | 2030 (w), 1937 (w), 1898 (vs), 1848 (s) |
| [(CO) ₅ CrI] ⁻ [(CH ₃ CH ₂) ₄ N] ⁺ | <i>a</i> | KBr | 2055 (w), 1930 (sh), 1914 (s), 1853 (m) |
| [(CO) ₅ CrCOCH ₃] ⁻ [(CH ₃) ₄ N] ⁺ | <i>b</i> | Nujol | 2041 (s), 1883 (vs) |
| [(CO) ₅ CrC(CF ₃)=CF(CF ₃)] ⁻ [(Ph ₃ P) ₂ N] ⁺ | 7a | THF | 2048 (w), 1920 (s), 1872 (m) |

^a E. W. Abel, I. S. Butler, and J. H. Reid, *J. Chem. Soc.*, 2068 (1963). ^b E. O. Fisher and A. Maasbol, *Chem. Ber.*, **100**, 2445 (1967).

(THF) at -78°. Treatment of this solution with excess DCl in diethyl ether gave monodeuterated carbene complex **1** (90% yield; 7.3% *d*₀, 90.0% *d*₁, 2.4% *d*₂, 0.6% *d*₃ by mass spectrometry). In a separate experiment, treatment of a solution of **2** with 1 equiv of bis(triphenylphosphine)iminium chloride⁵ in tetrahydrofuran followed by the addition of hexane resulted in the precipitation of a yellow (Ph₃P)₂N⁺ salt of the carbene anion (**3**) in 95% yield. Attempts to isolate lithium salt **2** have given pyrophoric residues; in contrast, the (Ph₃P)₂N⁺ salt (**3**) can be weighed in air, washed with water, and stored at 0° for several days with only slight decomposition.^{6,7}

The nmr and ir spectra of **3** indicate that the structure is best described as the vinylpentacarbonylchromium anion **3b**. The nmr spectrum of **3** in tetrahydrofuran-*d*₃ contains two one-proton singlets at δ 3.78 and 4.52⁸ due to the two nonequivalent vinyl hydrogens of **3b**, in addition to a methoxy singlet at δ 3.29 and a 30 H multiplet at δ 7.4–7.9 due to (Ph₃P)₂N⁺. The nmr spectrum of **3** remains unchanged up to 120° where rapid decomposition ensues and indicates a substantial rotational barrier about the carbon-carbon bond of **3**. The carbonyl stretching frequencies of anion **3** are all shifted to substantially lower frequency than their counterparts in carbene complex **1** and are similar to those observed for other substituted pentacarbonylchromium anions (Table I).

The very intense and widely separated ir bands of carbene complex **1** at 1941 cm⁻¹ and of the carbene anion **3** at 1898 cm⁻¹ allow the determination of the relative abundances of **1** and **3** in solution and therefore provide a means of determining the acidity of **1** relative to common acids. THF solutions containing **3** and acids of varying strength were prepared at low temperature and the relative concentrations of carbene complex **1** and of the carbene anion **3** were measured at 0° by ir spectroscopy. The carbene complex **1** is remarkably acidic. Neither 10 equiv of CH₃OH nor 10 equiv of diethyl malonate gave measurable protonation of **3**; 10 equiv of phenol gave a 30:70 ratio of **1**:**3** and 1 equiv of *p*-cyanophenol gave a 55:45 ratio of **1**:**3**. Thus, the thermodynamic acidity of **1** in THF is approximately the same as *p*-cyanophenol.

(5) J. K. Ruff, *Inorg. Syn.*, in press. We wish to thank Professor Ruff for a preprint describing the synthesis of (Ph₃P)₂N⁺Cl⁻.

(6) Appreciable decomposition occurs within several days at room temperature and made analysis difficult. *Anal.* Calcd for C₄₄H₃₆NO₆P₂Cr: C, 67.07; H, 4.49; N, 1.77; P, 7.86; Cr, 6.60. Found: C, 64.72; H, 4.94; N, 1.61; P, 7.38; Cr, 5.80.

(7) The bis(triphenylphosphine)iminium cation has been used in the isolation of stable salts of several otherwise unstable transition metal-carbonyl anions: (a) W. J. Schlientz and J. K. Ruff, *J. Organometal. Chem.*, **33**, C64 (1971); (b) W. O. Siegl and J. P. Collman, *J. Amer. Chem. Soc.*, **94**, 2516 (1972).

(8) For comparison, the two vinylic protons of the lithium enolate of *tert*-butyl acetate appear at δ 3.14 and 3.44 in benzene: M. W. Rathke and D. F. Sullivan, *J. Amer. Chem. Soc.*, **95**, 3050 (1973).

1 is one of the most acidic neutral carbon acids known. The high acidity of **1** can be understood in terms of resonance form **1b** which draws attention to the analogy between alkylalkoxycarbene complexes and positively charged O-alkylated ketones. The high acidity of **1** can also be ascribed in part to the delocalization of negative charge onto the electronegative oxygen atoms of the pentacarbonylchromium moiety in **3b**.

The lithium salt of the carbene anion **2** is more easily protonated than the corresponding [(Ph₃P)₂N]⁺ salt **3**. Thus, addition of 1 equiv of diethyl malonate to a freshly generated solution of lithium salt **2** gave a 65:35 mixture of **1**:**2** while addition of 10 equiv of methanol gave a 15:85 mixture of **1** and **2**. In the presence of 5 equiv of hexamethylphosphoric triamide (a reagent known for its ability to solvate Li⁺), the lithium salt **2** behaved similar to the (Ph₃P)₂N⁺ salt **3** and required *p*-cyanophenol to effect protonation. We attribute the different behavior of **2** and **3** to the stabilization of conjugate bases (methoxide, phenoxide) by lithium ion, which facilitates protonation of the carbene anion in its presence. The (Ph₃P)₂N⁺ cation cannot stabilize these conjugate bases by coordination. The nmr and ir spectra of **2** and **3** are identical except for absorptions due to the (Ph₃P)₂N⁺ cation; consequently, we believe that the carbene anion is solvent separated⁹ and not affected by the counterion.

Since metal-carbene complexes can readily be converted to esters by oxidation reactions,¹⁰ carbene anions are the synthetic equivalent of ester enolates. The carbene anions are only weakly basic in relation to ester enolates and can be generated under mild conditions. The synthetic utility of these weakly basic but reactive anions is under investigation.

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(9) Lithium tetracarbonylcobaltate (-I) exists as a solvent separated ion pair in THF: W. F. Edgell, J. Lyford, II, A. Barbetta, and C. I. Jose, *J. Amer. Chem. Soc.*, **93**, 6403 (1971).

(10) C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, **94**, 6543 (1972).

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Neutral Hydrolysis of *p*-Nitrophenyl Dichloroacetate in Highly Aqueous *tert*-Butyl Alcohol. Effects due to Solvent Structural Integrity

Sir:

Esters such as *p*-nitrophenyl dichloroacetate (**1**), which are activated by strong electron withdrawal in the