21, 499 (1970), and references therein.

(19) Variations in k_f with structure for β,γ-enones **1–6** may lead to changes in Φ_f but will have little effect on τ_f because $k_f \ll 1/\tau_f$ for these enones. The k_f values can be approximated from the electronic absorption spectrum. See, for example, N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1965, p 48.

(20) Similar τ_f values are observed by Schuster and co-workers for β,γ-enones **1–3**.[15]

(21) The only way the τ_f values for **1–3** can be consistent with 1,3-acyl shift from the $^1n,\pi^*$ state is if k_{st} decreases dramatically, e.g., by a factor of 50, in going from **1** to **3**. This seems highly unlikely in view of the small effects of α-methyl substitution on alkanone and β,γ-enone k_{st} values.[1e,9]

(22) A referee has noted that alkyl β,γ-enones which undergo the 1,3-acyl shift on direct irradiation do not always yield this reaction with acetone sensitization. He suggests that this creates a problem for the proposal that 1,3-acyl shifts can occur from the enone $^3n,\pi^*$ T_2 state. It seems likely to us, however, that the efficiency of energy transfer from the acetone $^3n,\pi^*$ state to the alkyl β,γ-enone $^3n,\pi^*T_2$ state will be very sensitive to the energy of the β,γ-enone T_2 state and hence may vary considerably from enone to enone.

(23) Note Added in Proof. For a related discussion, see K. Schaffner, *Tetrahedron*, **32**, 641 (1976).

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Photochemistry of Ketones in Solution. 50.[1] Fluorescence Lifetimes of β,γ-Unsaturated Ketones. Structural Dependence of Rate Constants for Reaction and Decay of Singlet Excited States

Sir:

The intense interest shown in recent years in the photochemistry of β,γ-unsaturated ketones (β,γ-UK) is a reflection of the many competing reaction pathways characteristic of these systems, a virtual microcosm of ketone and olefin photochemistry.[2] The subtle dependence of photochemical reactivity on structural features of these ketones has been particularly intriguing: alkyl substitution, ring enlargement, and conformational modifications often completely alter the reaction course.[2] The configuration and multiplicity of the several reactive excited states are also primary controlling factors.[2,3]

Attempts to account for the variation in reaction pathways between one system and another have been complicated and indeed thwarted by the lack of quantitative reactivity data.[2] As is well appreciated, the only valid way to judge reactivity for excited states is measurement of specific rate constants.[4] The singlet excited state lifetime τ_S is governed by the rate constants for fluorescence (k_f), radiationless decay to the ground state (k_{ds}), intersystem crossing to the triplet manifold

(k_{ST}), and reaction (k_r^S) according to eq 1. The rate constant k_i for any given process with quantum efficiency Φ_i is given by eq 2.

$$\tau_S^{-1} = k_f + k_{ds} + k_{ST} + k_r^S \qquad (1)$$

$$k_i = \Phi_i \tau_S^{-1} \qquad (2)$$

In an attempt to lend order to the bewildering array of factors which appear to govern the photoreactivity of β,γ-UK, we have measured the singlet lifetimes of a number of these ketones (shown below) by monitoring their fluorescence decays in fluid solution at room temperature.[5,6,7] All compounds were carefully and repeatedly purified using appropriate techniques (distillation, gas–liquid chromatography, liquid chromatography) to ensure that the observed fluorescence in each case was not derived from impurities. All ketones show broad structureless fluorescence in cyclohexane solution with maxima between 400 and 420 nm and excitation spectra (λ_{max} 300–315 nm) corresponding to the carbonyl n→π* transition. Quantum yields for fluorescence (Φ_f) were determined (λ_{ex} 313 nm) by comparison of corrected emission intensities with that of N,N,N',N'-tetramethyl-p-phenylenediamine (Φ_f = 0.18 in cyclohexane).[8] The fluorescence lifetimes in Table I were deterined by single photon counting with data treatment by computer convolution.[9,10]

Rate constants for various singlet-derived processes are given in Table I where quantum yield data are available from this and earlier work.[11] Values of k_{ST}, which are of particular interest, are calculated from values of Φ_{ST}, derived from eq 3 and 4,

$$\Phi_P^{dir} = \Phi_{ST}\Phi_R^T \qquad (3)$$

$$\Phi_P^{sens} = \Phi_{ST}^{sens}\Phi_{ET}\Phi_R^T \qquad (4)$$

where Φ_P^{dir} is the quantum efficiency for formation of triplet-derived products on direct photolysis of the ketone, and Φ_R^T is the fraction of ketone triplets which afford the product; Φ_P^{sens} represents the efficiency of forming the same product on triplet sensitization and equals Φ_R^T under conditions where the triplet yields of the sensitizer (Φ_{ST}^{sens}) and triplet energy transfer (Φ_{ET}) are each unity. In cases where the [1,2]-acyl shift product is not observed on direct photolysis, its yield is estimated to be less than 5% of the yield of the major observed product in order to provide an upper limit to k_{ST}.

It should be noted first of all that the values of k_f vary only slightly for this series of compounds, within a factor of 7, a point which was not established by previous studies.[2] Calculation of k_f directly from room temperature uv spectra of β,γ-UK gives values in good agreement with experiment.

The balance of this initial report will focus on the relation-

Table I. Fluorescence Lifetimes and Reactivity Data of β,γ-Unsaturated Ketones

Compd	τ_S, ns	Φ_f	k_f, s⁻¹	$k_{1,3}^S$,[a] s⁻¹ ($\Phi_{1,3}$)	k_{ST}(A),[b] s⁻¹ (Φ_{ST}^A)
1a	1.56 ± 0.05	2.1×10^{-3}	1.3×10^6	1.8×10^8 (0.28)[11a]	$<1.0 \times 10^8$ (<0.16)[11a]
1b	0.41 ± 0.05	9.6×10^{-4}	2.3×10^6	9.8×10^7 (0.04)[11a]	$<1.6 \times 10^8$ (<0.067)[11a]
3	0.66 ± 0.05	5.4×10^{-4}	8.2×10^5	1.5×10^7 (0.01)[11a]	2.5×10^8 (0.17)[11a]
1c	~ 0.1	4.6×10^{-4}	$\sim 4.6 \times 10^6$	c	d
1d	0.61 ± 0.05	9.2×10^{-4}	1.5×10^6	c	d
1e	0.47 ± 0.05	6.9×10^{-4}	1.5×10^6	c	d
2a	1.7 ± 0.1			$<5.9 \times 10^6$ (<0.01)[11b]	5.9×10^8 (1.0)[11b]
2b	2.4 ± 0.1			6.3×10^7 (0.15)[11b]	e
2c	3.4 ± 0.1			7.1×10^7 (0.24)[11b]	$<1.2 \times 10^8$ (<0.4)[11b]
4	2.25 ± 0.05	2.0×10^{-3}	8.9×10^5	5.8×10^7 (0.13)[11e]	d
5	5.0 ± 0.1	3.5×10^{-3}	7.0×10^5	6.0×10^6 (0.03)[11c]	d
6	4.91 ± 0.05	7.2×10^{-3}	1.5×10^6	d	d

[a] Rate constant for singlet-derived [1,3]-acyl shift required by mechanism A, assuming no partitioning of a biradical intermediate (see footnote 12). [b] Rate constant for intersystem crossing required by mechanism A (see text). [c] [1,3]-Acyl shift not observed. [d] Relevant quantum yield not reported. [e] Data indicate $\Phi_R^T < \Phi_P^{dir}$, inconsistent with eq 3.

ship of these data to the question of the mechanism of the [1,3]-sigmatropic acyl rearrangement, a reaction shown by most of the compounds we have studied, and a matter of intense current interest.[2,6] It has been universally concluded in the literature of this field,[2] until very recently, that this ubiquitous reaction of β,γ-UK occurs from the lowest singlet excited state S_1, since it is not quenched by high concentrations of triplet quenchers and is usually not observed on triplet sensitized photolysis. The values of $k_{1,3}{}^S$ in column 5 of Table I have been calculated on the basis of this mechanism (A).[12] In accord with rate constants for α-cleavage of excited alkanones[4b,15] values of $k_{1,3}{}^S$ show the expected increase upon alkyl substitution at the α-carbon, with a spread of approximately an order of magnitude, i.e., ~6 for **1b** vs. **3** and >12 for **2c** vs. **2a**.[12] There seems to be no disagreement with the conclusion that the [1,2]-sigmatropic acyl shift (oxadi-π-methane rearrangement)[16] originates from the lowest triplet state T_1,[2,16] which enables calculation (or estimation) of values of k_{ST} required by mechanism A, given in column 6 of Table I. Where direct comparisons are possible (**2c** vs. **2a**, **1b** vs. **3**), substitution by methyls at the α-carbon reduces k_{ST}, a trend previously observed for alkanones[4b,17] and 3-cyclopentenones.[18] The few values of k_{ST} determined to date do not provide a sufficiently general correlation between k_{ST} and molecular structure so as to allow a firm prediction about the direction and magnitude of change in k_{ST} upon structural variation. Nevertheless the observed changes in k_{ST} and $k_{1,3}$ are both precedented, so we have no basis for ruling out mechanism A.

An alternative mechanism (B) for the [1,3]-acyl shift is proposed in the accompanying paper by Dalton et al.[6] and has been independently suggested by Schaffner.[2c] This mechanism envisages the [1,3]-acyl shift as occurring from an upper triplet n,π^* state (T_2) following intersystem crossing, in which case the fluorescence lifetime is no longer coupled to the efficiency with which the ketone undergoes this reaction, i.e., $k_{1,3}{}^S$ $\ll \tau_s{}^{-1}$. This mechanism also has the virtue of rationalizing the occasional observation of triplet sensitized [1,3]-acyl shifts,[11a,19,20] although it must be kept in mind that there are also instances[2,16] where this reaction is not seen on acetone sensitization even though it occurs on direct photolysis. In mechanism B, there must then be a competition between reaction from T_2 (rate constant $k_{1,3}{}^T$) and decay (k_{dt}) to the lower π,π^* triplet (T_1) responsible for the [1,2]-shift.[21] The extremes are represented by those compounds without α-substituents which on direct irradiation undergo the [1,2]-acyl shift exclusively (e.g., **2a**) and those with two α-methyl groups which only undergo the [1,3]-acyl shift (e.g., **1a, 1b, 2c, 4**). Mechanism B requires that the ratio $k_{1,3}{}^T/k_{dt}$ must vary greatly, from <0.01 in the case of **2a** to >2 for **2c**; somewhat larger values are estimated for **1a, 1b**, and **3**, but are less reliable because of competing singlet free radical reactions.[11a]
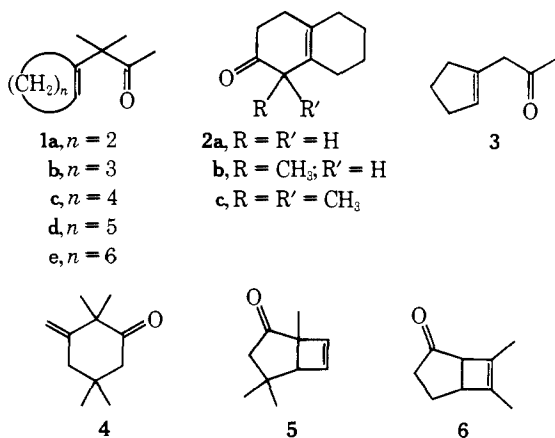
Although absolute values of $k_{1,3}{}^T$ and k_{dt} cannot be derived from the data, one would expect by analogy[4b,15] that $k_{1,3}{}^T$ ought to increase on α-methylation. It is important to note that these ratios of $k_{1,3}{}^T/k_{dt}$ (mechanism B) are comparable in magnitude to $k_{1,3}{}^S/k_{ST}$ (mechanism A), and their variation must be the result of similar structural effects on the competition between α-cleavage and radiationless processes in T_2 or S_1, in the two alternative mechanisms.

On the basis of our analysis, we feel that a definite choice between the two mechanisms described above is premature, particularly for octalones **2a–c**, and both mechanisms must be considered in interpreting results from the literature and in planning new studies. The data obtained in this study and by Dalton[6] provide a new quantitative framework in which these and other mechanisms must be evaluated, which is itself an important objective of our work.

1a, n = 2
b, n = 3
c, n = 4
d, n = 5
e, n = 6

2a, R = R′ = H
b, R = CH₃; R′ = H
c, R = R′ = CH₃

3

4   5   6

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(2) For a comprehensive review of all previous work in this field, see (a) K. N. Houk, *Chem. Rev.,* **76**, 1 (1976). See also (b) W. G. Dauben, G. Lodder, and J. Ipaktschi, *Top. Curr. Chem.,* **54** (1975); and (c) K. Schaffner, *Tetrahedron,* **32**, 641 (1976).

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(4) For specific illustrations, see (a) P. J. Wagner, *Acc. Chem. Res.,* **4**, 168 (1971); (b) J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Am. Chem. Soc.,* **92**, 2564 (1970).

(5) Other observations of fluorescence of β,γ-UK: (a) K. G. Hancock and R. O. Grider, *Tetrahedron Lett.,* 4281 (1971); (b) S. R. Kurowsky and H. Morrison, *J. Am. Chem. Soc.,* **94**, 507 (1972); (c) D. I. Schuster and C. W. Kim, *ibid.,* **96**, 7437 (1974).

(6) A related study utilizing this technique is described in the accompanying paper, J. C. Dalton, M. Shen, and J. J. Snyder, *J. Am. Chem. Soc.,* previous paper in this issue.

(7) A related study of bis-β,γ-UK including a number of 3,5-cycloheptadienones will be published separately by J.E. and D.I.S.

(8) I. B. Berlman in "Handbook of Fluorescence Spectra of Aromatic Molecules", 2d ed, Academic Press, New York, N.Y., 1971.

(9) A combination of Corning glass filter 7-54 and a 2 M solution of NiSO₄ in a 2-cm cell restricted excitation to 290–340 nm and emission was monitored at λ >405 nm using a 1-cm filter cell containing NaNO₂ (75 g/100 ml of H₂O). Sample solutions, OD 1–2, were purged with N₂ prior to each measurement. The fluorescence decay data[10] were analyzed with computer assistance by both iterative convolution[10b] and visual fitting on an x,y-recorder of the data to the decay calculated from trial lifetimes and the lamp profile measured in each run (nitrogen-filled lamp, width at half-height ~2 ns). Single exponential decays were observed in each instance, and lifetimes down to 0.1 ns could be determined reproducibly to within 0.05 ns.

(10) (a) W. R. Ware in "Creation and Detection of the Excited State", A. A. Lamola, Ed., Vol. 1, Part A, Marcel Dekker, New York, N.Y., 1971, Chapter 5; (b) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Am. Chem. Soc.,* **96**, 439 (1974).

(11) (a) P. S. Engel and M. A. Schexnayder, *J. Am. Chem. Soc.,* **97**, 145 (1975); (b) P. S. Engel, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *ibid.,* **96**, 924 (1974); (c) D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.,* 1661 (1970); (d) D. I. Schuster, J. T. Diehl, S. Hussain, and A. B. Gupta, unpublished results; (e) K. G. Hancock and R. O. Grider, *J. Am. Chem. Soc.,* **96**, 1158 (1974).

(12) We are assuming for this purpose that the (1,3)-acyl shift does not involve a biradical intermediate which can partition between formation of product and return to ground state ketone. In some acyclic analogues, partial trapping of radical intermediates in this reaction has been achieved.[13] Subsequent correction if necessary for any such wastage process[14] should involve only minor changes in $k_{1,3}$.

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(15) (a) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970), and references therein; (b) P. J. Wagner and R. W. Spoerke, *J. Am. Chem. Soc.*, **91**, 4437 (1969).
(16) For a review of this reaction, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
(17) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *J. . Chem. Soc.*, **92**, 6974 (1970).
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(19) (a) M. A. Schexnayder and P. S. Engel, *Tetrahedron Lett.*, 1153 (1975); (b) R. K. Murray and K. A. Babiak, *ibid.*, 319 (1974); (c) K. G. Hancock, J. T. Lau, and P. L. Wylie, *ibid.*, 4149 (1974); (d) R. K. Murray, D. L. Goff, and R. E. Ratych, *ibid.*, 763 (1975).
(20) There are obvious problems in accommodating the observations of triplet sensitized (1,3)-acyl shifts with mechanism A. One possibility, which seems to have been excluded in at least some studies,[11a,19] is that some direct excitation of the substrate ketone or singlet energy transfer occurs. Another possibility involves reaction from T$_2$ in the sensitized photolysis and from S$_1$ on direct excitation. Still another involves thermal population of S$_1$ from the triplet manifold, a process known to occur for benzophenone at room temperature.[21]
(21) J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *J. Am. Chem. Soc.*, **92**, 410 (1970).
(22) There appears to be general agreement that the lowest triplet state has a dominantly π,π^* configuration,[2a,3b,c] even though the reported phosphorescence of a number of β,γ-UK[23] which supported this conclusion could not be verified using highly purified ketones.[19a,24]
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(24) P. S. Engel, M. A. Schexnayder, W. V. Philips, H. Ziffer, and J. I. Seeman, *Tetrahedron Lett.*, 1157 (1975).

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Stabilization of Carbonyl Clusters by a Carbide Atom. Synthesis and Characterization of [Co$_8$(CO)$_{18}$C]$^{2-}$ and of Paramagnetic [Co$_6$(CO)$_{14}$C]$^-$ Anions

Sir:

The synthesis of the dianion [Co$_6$(CO)$_{15}$C]$^{2-}$, which is isostructural with the trigonal prismatic [Rh$_6$(CO)$_{15}$C]$^{2-}$, has previously been reported.[1] We now wish to report the ^{13}C NMR spectra of [Co$_6$(CO)$_{15}$C]$^{2-}$, and to report on its transformation into the new anions [Co$_6$(CO)$_{14}$C]$^-$ and [Co$_8$(CO)$_{18}$C]$^{2-}$.

Samples of [Co$_6$(CO)$_{15}$C]$^{2-}$ (ca. 30% ^{13}CO) have been prepared both starting from equally enriched Co$_3$(^{13}CO)$_9$CCl and Na[Co(^{13}CO)$_4$] and also from Co$_3$(CO)$_9$CCl and Na-[Co(^{13}CO)$_4$]. In both cases the ^{13}C NMR spectra at $-70°$ in perdeuterioacetone are very similar and consist of three signals of relative intensities 3:6:1.4 assigned to edge-bridging (δ 252 and 234.9 ppm; $\omega_{1/2}$ 76 Hz) and terminal carbonyls (δ 224.9 ppm; $\omega_{1/2}$ 13 Hz), respectively. In agreement with the similarity in the solution ir spectra of the two dianions,[1,2] this pattern is similar to that previously found for [Rh$_6$-(CO)$_{15}$C]$^{2-}$.[3] The considerable deviation from the expected intensities (3:6:6) is probably related to the anomalous relative intensities found in Co$_4$(CO)$_{12}$,[4] and confirms that intensities in the ^{13}C NMR spectra of cobalt compounds should be interpreted with care.

The ^{13}C NMR spectrum of [Co$_6$(CO)$_{15}$^{13}C]$^{2-}$ (ca. 90% ^{13}C$_{carbide}$)[5] in perdeuterioacetone at $-70°$ is similar to those reported above except for the presence of the carbide resonance at 330.5 ppm ($\omega_{1/2}$ 43 Hz), thus proving the source of the carbide atom (^{13}CCl$_4$) and showing a considerable shift to lower field in comparison with the corresponding rhodium analogue (δ 266.7 ppm).[3]
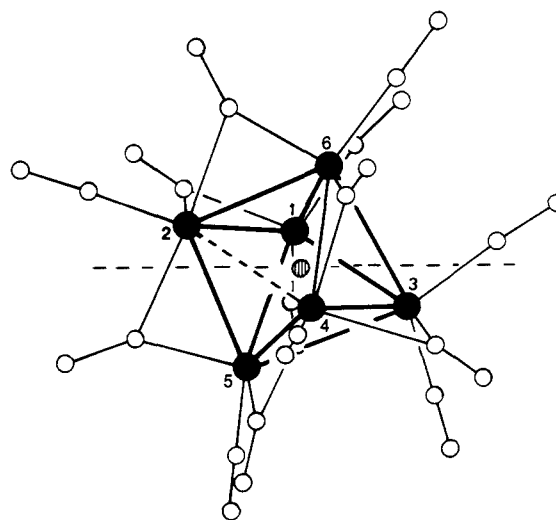

Figure 1. Structure of the [Co$_6$(CO)$_{14}$C]$^-$ anion. The idealized twofold axis is shown. The cobalt–cobalt distances have the following values (Å): 2–4, 2.96 (1); 1–2, 2–5, 2–6, 3–4, 4–5, and 4–6, 2.53 (mean); 1–3, 1–5, 1–6, 3–5, and 3–6, 2.75 (mean).

Solutions of the Na$^+$ or [NMe$_3$(CH$_2$Ph)]$^+$ salts of [Co$_6$(CO)$_{15}$C]$^{2-}$ in THF react with carbon monoxide (1 atm, 25°)[6] to give a mixture of compounds containing the anion [Co(CO)$_4$]$^-$, Co$_2$(CO)$_8$, Co$_4$(CO)$_{12}$, some Co$_3$(CO)$_9$CX derivatives (X not yet identified), and the new dark brown paramagnetic anion [Co$_6$(CO)$_{14}$C]$^-$. More conveniently this new anion has been isolated (10–20% yield) in a pure form as the Na$^+$, [NMe$_4$]$^+$, and [NEt$_4$]$^+$ salts by reaction of Co$_3$(CO)$_9$CCl with 2 mol of Na[Co(CO)$_4$] in diethyl ether; the ir spectrum (THF) shows carbonyl stretching absorptions due to both terminal (2070 vw, 2020 vs, and 1990 sh cm^{-1}) and bridging (1857 s cm^{-1}) groups. The ESR spectrum (THF) shows a strong signal at g = 2.0128 and the paramagnetism has been confirmed using Evans' method[7] ($\mu_{eff} \simeq 1.37\ \mu_B$).

Since there are no previous reports of stable hexanuclear paramagnetic carbonyls, we have carried out an x-ray structural determination.[8] The structure is shown in Figure 1 and provides further evidence for the presence of an unpaired electron in excess to the usual 86 found in hexanuclear carbonyl clusters of octahedral structure.[9] The metal atom cluster is a distorted octahedron of idealized molecular symmetry C_{2v}. The 12 cobalt–cobalt interactions can be divided into three sets: one stretched edge 2.96 (1) Å, six carbonyl-bridged edges of mean length 2.53 Å, and five edges of intermediate lengths (mean 2.75 Å). The Co–C carbide distances are in the range 1.84–1.94 (2) Å, with mean value of 1.88 Å.

The reaction of the dianion [Co$_6$(CO)$_{15}$C]$^{2-}$ with Co$_4$(CO)$_{12}$ provides a further example of a redox condensation reaction:[9]

$$2[Co_6(CO)_{15}C]^{2-} + Co_4(CO)_{12} \xrightarrow[i-Pr_2O]{60°}$$
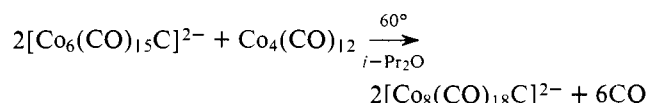
$$2[Co_8(CO)_{18}C]^{2-} + 6CO$$

The diamagnetic octanuclear dianion has been isolated (~80% yield) as pure Na$^+$ and [NMe$_3$(CH$_2$Ph)]$^+$ salts; the ir spectrum (THF) shows carbonyl stretching absorptions at 2055 vw, 1990 vs, 1950 w, and 1810 m cm^{-1}.

The structure[10] of the dianion [Co$_8$(CO)$_{18}$C]$^{2-}$ is shown in Figure 2. The metal atom polyhedron can be described as a tetragonal antiprism elongated along one of the two-fold symmetry axes, resulting in the idealized symmetry D_2. The Co–Co distances are in the range 2.47–2.59 (1) Å with mean value of 2.52 Å; there are no significant differences between the basal and the interbasal distances. The carbide atom is in the center of the cluster but, due to the previously mentioned