Table I. Products of Carbenoid Thermal Decomposition

		Reaction conditions^a — T, °C (t, hr) —		— % products^b —		
Entry	Carbenoid	A	B	**4**	**5**	**6**
1	**1b**^{c}	−8 (0.3)	0 (2)	80	Trace	
2	**2b**^{d}	−10 (0.2)		26	Trace	
3	**2b**^{e}	−78 (1)	22 (1.5)	92	3	
4	**3b**^{f}	−78 (2.5)	10 (1)	1	27	61
5	**3b**^{g}	−16 (0.2)	−10 (0.5)	23	24	~5

[a] Carbenoids were prepared by exchange with ethereal methyllithium (no LiBr unless noted) and stirred at temperature A for the indicated time, followed by stirring at temperature B and quenching with methanol or water at the indicated time. [b] Yields (±2%) were determined by vpc using internal standards unless otherwise indicated. [c] Methyllithium–LiBr used; other products: **1c** (4%), **1d** (6%). [d] Prepared from **2a** and butyllithium; other products: **2c** (54%), two butyl-containing unknowns (~20%). [e] Prepared from **2d**, other products: **2c** (trace). [f] Yields determined by isolation plus vpc; other products: **3c** (1–2%), three unknowns (total 4–5%). [g] Reaction run using methyllithium–LiBr; other products: **1c** (13%), **2c** (3%), **3c** (5%); yield of **6** by isolation.

formation temperatures carbenoid **3b**, when prepared in the absence of LiBr, gave reduced yields of dimers **6** and higher yields of **5** but never more than 3% of **4**. The loss of stereoselectivity in the thermal reactions of carbenoid **3b** (entry 5, Table I) when LiBr is present may well be due entirely to halide exchange with concomitant carbenoid isomerization. The presence of bromide ion had little effect on the stereochemistry of the thermal reaction of bromocarbenoid **1b**. Carbenoid **2b** has yet to be tested in the presence of bromide ion.

The above results complement the deuterium isotope results of Goldstein and Dolbier[4] and further indicate that in the transition state of α elimination LiX is bound to carbon tightly enough to influence the stereochemical outcome of these electrophilic reactions.

In the above we have emphasized the stereochemical difference at C-8 between **2b** and **3b**. It should be noted that these carbenoids differ in thermal stability and, most probably, in state of aggregation and conformation as well. The role of the first two effects is not understood but the importance of the last effect on intramolecular C–H insertion reactions of "cyclopropylidines" is well documented.[8] Thus, if both oxygen atoms are coordinated with Li in **2b**, then the resulting conformation of **2b** (as shown) should preclude insertion at C-2 (or C-6). However, expecting that **3b** should have a conformation similar to that of **3a** which, by nmr, is different from that shown, we conclude that intramolecular C–H insertion at C-2 and C-4 (or C-6) is not conformationally precluded and that other factors, among them the stereochemistry at C-8, must dictate the product distribution.

Finally, while with the present carbon skeleton C–H insertion cleanly takes place on the side opposite the departing halogen, this may not be generally true. For example, we have already observed that carbenoid **7** yields C–H insertion at C-5 in 51% yield.[1b] Further work on the stereochemistry of reactions of **2b** and **3b** at higher temperatures is in progress.

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Lifetime of the $^4T_{2g}$ State of Tris(2,4-pentanedionato)chromium(III) Reexamined

Sir:

Observation of a relatively rapid relaxation between the ^1A and ^5T states of an iron(II) complex[1] has prompted reexamination of slower intersystem crossing processes reported for metal complexes. A rate constant of 1.2×10^5 sec^{-1} for intersystem crossing from the photoexcited $^4T_{2g}$ state to the ^2E_g state of Cr(acac)$_3$ has been inferred[2] from an apparent maximum in the observed luminescence intensity as a function of time at 77°K. We have reinvestigated the luminescence of this complex and find no evidence of such a maximum. Under the conditions of our experiment, this implies a lower limit of 10^7 sec^{-1} for the rate constant for intersystem crossing to the ^2E_g state.

Tris(2,4-pentanedionato)chromium(III)[3] was purified by recrystallization and characterized by elemental analyses and its visible absorption spectrum.[4] A 10^{-2} *M* solution in 1:1 methanol–ethanol was degassed and sealed *in vacuo* in a silica cell which was immersed directly in liquid nitrogen to form a clear glass. A pulsed dye laser was used as the excitation source.[5] The output wavelength of the dye laser was determined with a Spex 1700 III spectrograph to be 593 nm with a band width of 2 nm. The luminescence was observed through a Corning 2-64 filter and a Jarrell-Ash 1/4 meter monochromator with a spectral band width of approximately 30 nm. An RCA C31034A photomultiplier tube with a flat relative sensitivity to 840 nm and a Tektronix 454 oscilloscope with a photodiode external trigger completed the detection system.

Typical results are presented in Figure 1. On the slowest time scale, Figure 1c, a phosphorescence decay is observed with a lifetime at 431 ± 9 μsec, corresponding to a rate constant of 2.3×10^4 sec^{-1} at 77°K. This is in excellent agreement with the lifetime of 420 μsec reported[6] at 85°K but somewhat longer than the lifetime of 360 μsec previously reported[2] at 77°K. We observed lifetimes as short as 180 μsec in preliminary experiments when the sample was not directly immersed in liquid nitrogen but was cooled by thermal contact with a reservoir at 77°K. This reflects the expected temperature dependence of the phosphorescence lifetime and suggests that in the previous experiment[2] the sample temperature was somewhat greater than 77°K. The wavelength of maximum luminescence was observed to be 785 nm, in good agreement with the reported[7] value of 777 nm, considering the wide band

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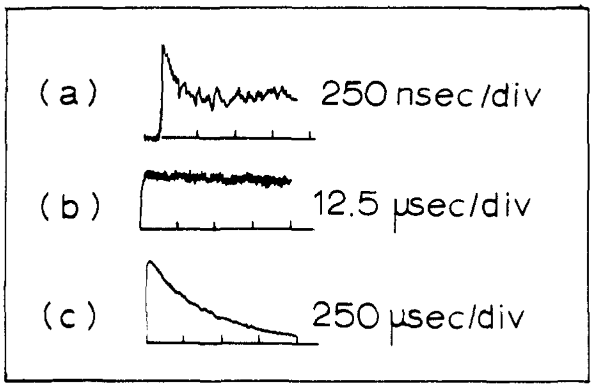

Figure 1. Luminescence intensity against time for $Cr(acac)_3$ at 77°K. Excitation wavelength is 593 nm; observation wavelength is 785 nm. Intensity units are arbitrary. RC time constants: (a) 25 nsec; (b) 500 nsec; (c) 5 μsec.

width of the monochromator and the improved red response of the photomultiplier employed. These results confirm that we have indeed observed the well-characterized phosphorescence of $Cr(acac)_3$.

There is no evidence for a maximum in luminescence intensity *vs.* time records. As shown in Figure 1b, on the time scale for which a maximum was previously reported, only a luminescence decay is observed with a lifetime of the phosphorescence decay within experimental error. At the fastest sweep rate used, Figure 1a, a rapid decay is observed, presumably due to scattered light from the laser, but no increase in luminescence intensity is observed. This requires that the ^2E_g state, from which phosphorescence occurs, is populated with a rate constant of 10^7 sec^{-1} or greater.

Our result implies that the intersystem crossing process is facile and that the lifetime of the $^4T_{2g}$ state is relatively short if crossing to a lower energy ^2E_g state is possible. It does not exclude a primary role for the $^4T_{2g}$ state in subsequent photochemistry since back thermal intersystem crossing from the ^2E_g to the $^4T_{2g}$ state could be equally facile.[8]

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Substitution Reactions of 1,1′-Dimethoxyuranocene and 1,1′-Bis(uranocyl)trimethylammonium Iodide with Organolithium Reagents[1]

Sir:

Uranocene, di-π-cyclooctatetraeneuranium, appears to be an f-orbital aromatic system homologous to the d-transition metallocenes;[2–4] however, the only reactions observed thus far with this new system are those at uranium[3] and at substituent groups.[5] We now report the first clear-cut reaction on the ligand rings.

1,1′-Dimethoxyuranocene[6] was prepared from methoxycyclooctatetraene[7] by conversion to the dianion and treatment with UCl_4 in THF. Structure assignment follows from analytical and spectral data;[8] for example, the visible spectrum shows four bands at λ_{max} nm (ϵ) 634 (860), 657 (540), 686 (460), and 698 (100), with the expected bathochromic shift[5] relative to uranocene. Furthermore, in common with the parent compound[3] and all other substituted uranocenes[5] studied, controlled air oxidation liberates the ligand rings in high yield. Stirring the dimethoxy compound with excess *n*-butyllithium in cyclohexane for 3 days at room temperature gives conversion to 1,1′-dibutyluranocene[5] in 70% yield. Similarly, *tert*-butyllithium gives 64% of 1,1′-di-*tert*-butyluranocene which was characterized by its mass spectrum (parent peak m/e 558) and visible absorption at λ_{max} nm (ϵ) 624 (1420), 652 (385), 671 (260), and 684 (125). The yields given are isolated yields of purified product. Phenyllithium, methyllithium, and lithium amide gave only unreacted starting material even after reaction periods of 7 days.

N,N-Dimethylaminocyclooctatetraene[9] was converted to the corresponding uranocene derivative.[8] Reaction with methyl iodide in THF for 24 hr gave the bistrimethylammonium iodide, $U(C_8H_7NMe_3^+I^-)_2$, as an insoluble crystalline material that was characterized by elemental analysis, and by the infrared spectrum which is similar to those of known uranocene derivatives. This compound also reacts readily with either *n*-butyllithium or *tert*-butyllithium to give the corresponding 1,1′-dialkyluranocene in 59 and 67% yields, respectively. However, the ammonium salt also reacts with phenyllithium to give 45% of 1,1′-diphenyluranocene[5] and with methyllithium to give 52% of 1,1′-dimethyluranocene.

The most reasonable reaction mechanism appears to involve a carbanion chain sequence initiated by metalation of the substituted uranocene at the position adjacent to the heterosubstituent and involving as an intermediate a uranium complex of cyclooctatrienyne.

This mechanism accounts for the sensitivity of the reaction to the effective basicity of the alkyllithium. Cyclooctatrienyne is a well-established intermediate in reactions of bromocyclooctatetraene with strong bases.[10] Direct nucleophilic substitution at the ligand

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