

The dynamics of the Ramdas layer[†]

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A little more than sixty years ago, the late L. A. Ramdas discovered a curious atmospheric phenomenon which had not been satisfactorily explained till recently. The phenomenon is the observation of a temperature minimum some 20–50 cm above bare soil on calm, clear nights. The first reports of these observations were treated with much scepticism, as the prevailing view was that the nocturnal temperature minimum always occurs at ground. In the present address the history of work on the lifted temperature minimum is traced and a new explanation is offered. It is emphasized that in this as well as many other phenomena, it is important to account for surfaces that are not perfectly black radiatively, i.e. those whose emissivity is not unity.

THE theme of this address is a curious atmospheric phenomenon whose study has a history dating back to the 1930s and has involved several Fellows of the Academy. Part of the lecture is going to recount just the story of the discovery and investigation of the phenomenon, which I find fascinating, and the rest is devoted to an explanation that I and my colleagues have proposed recently¹.

The person who made the discovery, and studied it over a period of about two decades, was L. A. Ramdas (1900–1979; Figure 1)², who was a Foundation Fellow of the Indian Academy of Sciences. Ramdas was one of C. V. Raman's many students who joined the India Meteorological Department (IMD), in those days virtually the only non-academic public agency in the country that had any use for scientists. Ramdas was a pioneer in agricultural meteorology: in 1931, a year after he was posted to Poona, he began a project on *Weather in Relation to Crops* at the initiative of the Imperial (as it was then known) Council of Agricultural Research. This project later flowered into the 'Agri Met' Division of IMD, among the first such to be set up anywhere in the world. Ramdas became internationally known for the many fundamental studies he made in the subject, and is extensively cited in Geiger's monumental work *The Climate near the Ground*³. He was therefore the father of agricultural meteorology in India, and would be one of a few founding fathers of the subject in the world as a whole. He retired as Deputy Director General of Observatories in 1956, but continued for many years thereafter at the National Physical Laboratory.

In 1932, with his young colleague Atmanathan, Ramdas published a two-page paper in the German journal Gerland's *Beiträge zur Geophysik*⁴, reporting that 'in the cold season [in India], the ground is at a higher



Figure 1. L. A. Ramdas (1900–1979).

temperature than the air immediately above' during clear nights. There are several interesting points in the paper (which by the way is reproduced in entirety in ref. 5). Measurements are quoted at four Indian stations, namely Poona, Agra, Madras and Bhadrachalam. The Poona data ('over dry ground') were presumably taken by the authors themselves at the Observatory; those at Agra are said to have been taken at the authors' request by Venkiteswaran⁶ (FASc, 1905–1985; joined IMD in 1930, and worked at the National Aeronautical Laboratory and the Tata Institute of Fundamental Research after retirement). I reproduce here as Figure 2 observations at

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three sites in Poona that illustrate the phenomenon; these observations were taken 'within a few days of its first detection'⁷, and are in fact more typical than the very first data that were published in ref. 4, for reasons that will become clear later.

Now it is common knowledge that temperature normally falls with altitude, the gradient (called the lapse rate) being about 6° per kilometre in the lowest kilometres of the atmosphere. It is also well known that very near the ground—in the lowest *centimetres*—the lapse rate can be orders of magnitude higher—a phenomenon incidentally investigated, also in 1932, by Ramdas in collaboration with Malurkar⁸ (FASc; 1903–1984). The general understanding at the time, as summarized e.g. in the well-known text of David Brunt⁹, was that at night the 'normal decrease of temperature [with altitude in the free atmosphere] may be replaced by a condition in which temperature steadily increased from the ground upward, giving what is known as an *inversion* in the lower layers, above which there is a return to the more normal decrease with height'; in other words, according to Brunt, the temperature distribution is generally like the curve A in Figure 3. What Ramdas and Atmanathan claimed was that on calm clear nights there was a further kink in the distribution, as in curve B in Figure 3.

The authors appear to have seen the phenomenon as special or peculiar to India and the tropics. The generally prevailing view that at night temperatures are lowest at ground is, the authors say, '... no doubt true for temperate latitudes. ... But in India. ...'. At another point in the paper they write, '... in the tropics the ground heating is so strong during day-time ...'. They finally

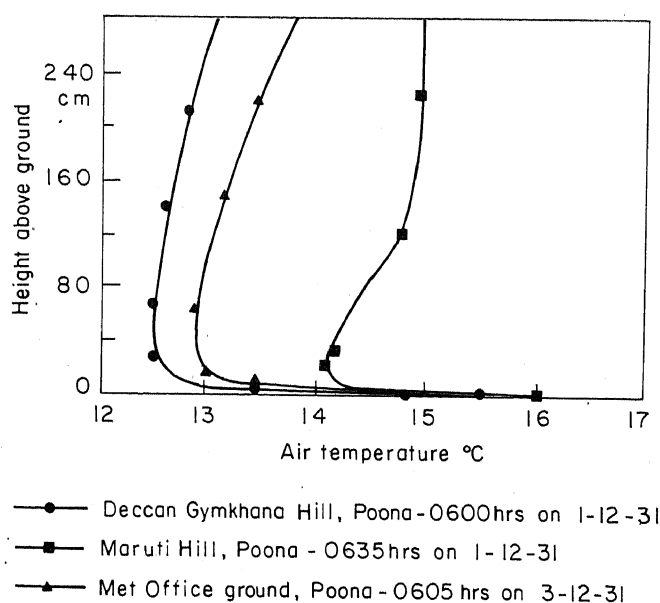


Figure 2. Temperature profiles near ground, measured at three sites in Poona (reproduced from Ramdas⁷).

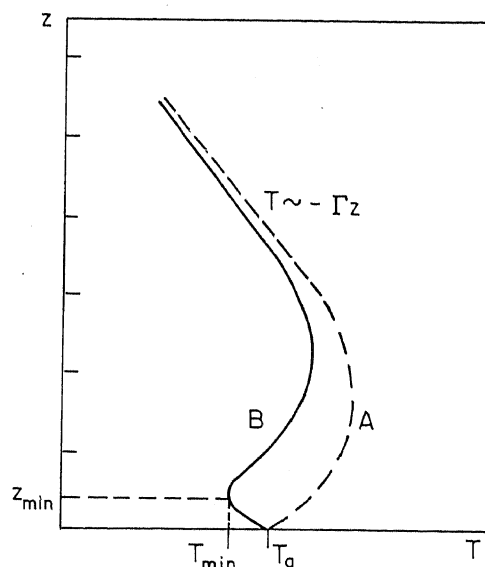


Figure 3. Temperature distribution near ground at night, as generally expected (curve A) and as found by Ramdas under calm, clear conditions (curve B).

remark that the data reported by them 'have raised some interesting problems regarding the role of radiation from the ground and the lower layers of the atmosphere'.

Lake¹⁰ has suggested that the lifted or elevated temperature minimum may have been observed by Glaisher¹¹ as far back as 1847. A careful examination of the long tables in this paper shows certain rare occasions when air temperature at a height of 4 ft was lower than on grass and some other surfaces. Unfortunately Glaisher did not discuss these differences in the text, so it is difficult to decide whether he had observed a lifted temperature minimum of the same type as Ramdas—there are actually several types, as we shall discuss shortly. Lake also cites a report by Cox in the US, dated 1910, that temperature measured 5 inches above bare soil in Wisconsin was often lower than that at the surface on clear nights. Ramdas and his colleagues, who were clearly unaware of this work, provided not only the first detailed temperature profiles that unambiguously established the existence of an unsuspected minimum, but also the earliest discussion of the physical principles that may govern the phenomenon.

In fact the report of Ramdas and Atmanathan was met with much scepticism, for several pertinent reasons. In the first place, the general understanding, as we have already seen, and as set forth even in later books on micro-meteorology (e.g. Sutton, ref. 12), was that there is always a nocturnal inversion at ground. This view is apparently supported by measurements, but in actual fact in many of these cases the measurements stop at the screen height of 1.2 m, and so do not necessarily contradict Ramdas and Atmanathan's conclusions about the temperature distribution *below* that height. Secondly, if ground is not coldest, there is a layer of heavy air on top of a lighter one; given the extremely high lapse

rates near ground, Rayleigh numbers based on the height of the temperature minimum (20–50 cm usually) and the corresponding temperature differential (several degrees) can be a factor of 100 or more times the critical values usually quoted for onset of Rayleigh–Benard thermal convection. So even if a temperature minimum were to form above ground, one might expect it to be overturned by convective instability. Finally, accurate temperature measurements near ground are not easy to make, so it was not clear whether the instruments used had been adequate. For all these reasons it is perhaps not entirely surprising that Geiger³ remarked in his treatise, ‘These results [of Ramdas] were at first accepted with reservations’; in an earlier German edition of the book¹³ he had declared that ‘the repetition of measurements which lead to such distributions is essential’.

The favoured explanation for the lifted temperature minimum (as we shall call the phenomenon) was that it must be due to advection, i.e. to the flow of colder air from the environs—draining down neighbouring slopes or passing through vegetation. Although Ramdas and Atmanathan admitted that this was a possibility in the case of the Poona measurements they reported in 1932, Ramdas quickly made the other measurements at two hill-tops in Poona⁷ that we have shown in Figure 2; advection could not have been a factor here, so one must seek other explanations. In fact during the next two decades he studied the phenomenon extensively¹⁴, charting the course of variation of the characteristics of the cold layer through the night, and demonstrating a continuity of behaviour over 24 hours. Given his background in optics (acquired working in Raman’s laboratory), he introduced the concept of what he called the ‘shimmering layer’—as it is thermal convection in this layer close to hot ground on a warm day that is responsible for the familiar shimmering of distant objects seen close to ground. He studied convection on a hot plate in the laboratory with Malurkar⁸, and saw the cold layer at night as the remnant of the shimmering layer during the day, with an inversion intervening between this cold layer and the temperature lapse in the free atmosphere. He reviewed the work he had done in a presidential address to the Science Congress (Physics Section) in 1948, in a paper¹⁵ in the *Archiv für Meteorologie, Geophysik und Bioklimatologie* in 1951, in another (dedicated to K. R. Ramanathan on his 60th birthday)¹⁴ in 1953 and in a Technical Note⁷ of the World Meteorological Organization in 1968. In his 1951 review, he still spoke of phenomena ‘which occur rather conspicuously in tropical and sub-tropical micro-climates’.

In the mid-fifties there appears to have been a sudden surge of interest in the subject, especially abroad. Lifted temperature minima were reported by workers in Argentina, USA, UK and several other countries³, showing that the phenomenon was by no means confined to the tropics. In particular Lake wrote two papers^{10, 16} on the

subject; the second evoked an interesting discussion¹⁰ in a meeting of the Royal Meteorological Society held in 1956, where doubts were expressed on Lake’s own observations of the lifted minimum (his temperature sensors were generally covered with water or ice). Scorer asked, ‘Could the radiation experts tell us what they can and cannot explain with realistic models?’, and did not receive an answer. Sutcliffe said he ‘would like to see differential equations set up in order to discuss whether values can be given to the parameters to permit the observed profiles to occur’.

Interestingly, the most convincing observations of lifted temperature minima came again from India and were published in 1957 by Klaus Raschke¹⁷, a young German agronomist who spent three years with Ramdas in Poona on a scholarship from the Indo-German Industrial Cooperation Scheme. Raschke took up Geiger’s suggestion that the earlier measurements must be repeated, and carried out a series of careful and thorough measurements that settled the question once and for all and are a landmark in the field. He made special thermoelectric sensors to measure air temperature (described in the Academy’s Proceedings¹⁸), and took care to compensate for the (small) radiation error they were subject to¹⁹. Based on his observations he distinguished between three different types of temperature distribution near ground: (i) the normal radiative type, with minimum temperature at ground, occurring on clear nights with wind; (ii) the special or singular radiative type (studied by Ramdas), with temperature minimum at a height of some decimeters above ground, occurring on calm, clear nights; and (iii) the advective type, with temperature minimum at some height above ground, occurring on clear or cloudy nights with advection of colder air. Types (ii) and (iii) were differentiated by the presence, in the former, of large temperature fluctuations at a height of about 1 m (which could be characteristic of Ramdas’s shimmering layer) and large temperature differences between 1 m and 10 m. (Incidentally these differences were so strong that Raschke could identify the type—(ii) or (iii)—without even making detailed profile measurements; this is significant as the very existence of type (ii) had been questioned.) To eliminate the possibility of advection, Raschke also made measurements on the remarkably flat top of Chaturshringi Hill in Poona. Reporting on observations made on 183 nights during 1953–54, Raschke found that during the calm winter months, type (ii) (i.e. the Ramdas type) was the one that generally prevailed. With the advance of season towards the monsoons, however, things gradually changed. Thus, while in November 1954 type (ii) was seen 98% of the time and the normal radiative type (i) only 2% of the time (the advective type (iii) was never observed, but the sample size was small), in June 1955 the figures had changed to 5, 38 and 57% respectively. The existence of the Ramdas type was

thus established beyond doubt. In one set of measurements (not on Chaturshringi Hill) where the lifted minimum could have been attributed to advection in the form of a tongue of cold air issuing from a sugarcane field 60 m away, its occurrence even after harvest served to rule out advection as the cause.

The Ramdas minimum is very sensitive to turbulent transport: Raschke could get rid of it by waving a plywood sheet nearby (thereby tripping the flow to a turbulent state, or at any rate increasing turbulent transport; see Figure 4). Transitions between the special and the normal type occur in minutes: Raschke records an instance where the temperature rose 5°C in a 3-minute interval!

There has till recently been no completely satisfactory explanation of the phenomenon. The generally accepted view not long ago (e.g. Sutton¹²) was that the cooling of air near the ground was basically a balance between conduction and convection, the radiative heat loss being confined to the surface. Möller²⁰ asserted that 'radiation processes are meaningless for the behaviour of the air layer near the ground', and considered the formation of fog or advection essential for the occurrence of the lifted minimum. Lettau²¹ advocated convection as the mechanism. Nevertheless, following the suggestion of Ramanathan and Ramdas²², radiation has often been thought to be responsible in some way^{10, 23, 24} (raising the immediate question where a length scale of 10–20 cm is relevant in atmospheric radiation). The only quantitative analysis of the problem till recently has been due to Zdunkowski²⁵, who followed up the suggestion by Möller that a haze layer above ground could lead to the strong radiative cooling that might explain the phenomenon. However, the theoretical temperature profiles presented by Zdunkowski were based on values of thermal diffusivity *lower* than the molecular value by a factor of up to 18; no results were presented for realistic values of the parameter. In this respect these results recall a calculation made by Ramdas and Malur-

kar⁸ who also had to assume very low diffusivities (factor of 22) to reproduce the observed steep temperature gradients near the surface (even in the absence of a lifted minimum). There is of course no way that molecular transport can be suppressed, so these unrealistically low diffusivities can only be interpreted as evidence of serious flaws in the theory. In any case, Raschke found no evidence of fog or haze near the ground when he observed a lifted minimum; neither did Oke²⁶, who made extensive measurements in Canada after the publication of Zdunkowski's paper. (We do often see a thin layer of fog suspended a foot or two above ground; this must therefore be a *consequence* of the lifted minimum, not its cause.) Finally, in Zdunkowski's results (e.g. in his figures 3 and 5) the minimum, when found, is rather flat, and takes the form of a nearly isothermal layer whose top coincides with the assumed upper edge of the haze layer, suggesting that the discontinuity in the modeled emissivity profile is largely responsible for the prediction of the lifted minimum.

If radiation does play a role it must be subtle. To see this suppose the medium is optically thick, then a flux-gradient relation for radiative transfer would be valid, and the net effect on the energy balance would be the same as an enhancement of thermal diffusivity. This renders the governing equation for the evolution of the temperature profile parabolic; and it can then be proved²⁷ that no lifted minimum can be sustained. If on the other hand the medium is optically thin, radiation just escapes across, and cannot affect the medium. Thus in neither of the two obvious limits can radiation explain the phenomenon. If therefore it holds the key, we must seek it in the peculiar properties of atmospheric absorption. Most of this is due to water vapour, but the absorptivity is a wild function of the wavelength, leading to a variation of the photon mean free path from a few metres in the strongly absorbing bands (wavelengths less than 8 μ or greater than 25 μ) to kilometres in the atmospheric window (8–14 μ)²⁸. This wide range of lengths makes the optically thick and thin limits very unrealistic and totally unhelpful.

We have recently completed extensive studies of a model that appears to offer a logical explanation of the phenomenon¹. This theory does not invoke a haze layer, but shows that one factor ignored in all previous explanations plays a key role. This is the surface emissivity (ϵ_g , say). In meteorological investigations it is usual to assume that the ground is radiatively black; it is indeed nearly so, but the small departures present do matter for a special reason⁵. The flux emissivity of the air, ϵ_a say, varies extremely rapidly with distance above ground (z) as the water vapour present in air is a strong absorber (especially in the rotation bands); the variation of ϵ_a with optical path is shown in Figure 5, and incidentally reveals the existence of what we shall call an 'emissivity sublayer' whose thickness (inversely pro-

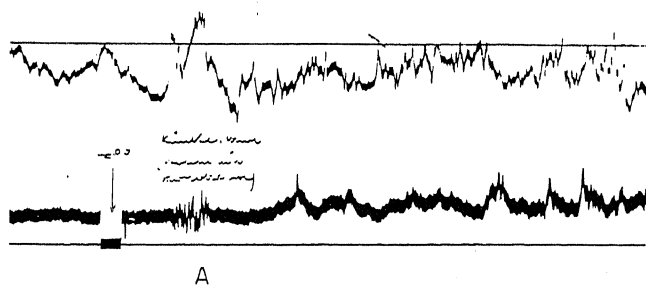


Figure 4. One of Raschke's records of the variation of the temperature differential between 1 mm and 10 mm above ground (top trace), and of wind velocity (bottom trace), taken in Poona during 1954–55. Note that when the intensity of velocity fluctuations (and hence turbulent transport) increases, as at A, the differential becomes positive, indicating disappearance of the lifted temperature minimum. (By the kind courtesy of Dr K. Raschke.)

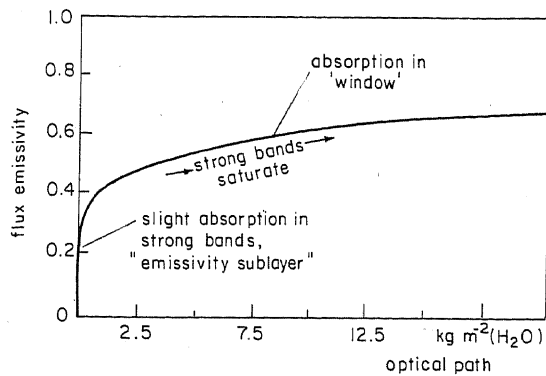


Figure 5. Variation of the flux emissivity of air with the optical path, showing rapid variation in an 'emissivity sublayer' near ground.

portional to $d\epsilon_a/dz$ at $z=0$, ≈ 1 m at a water vapour density of 10^{-2} kg/m^3) provides the hitherto missing length scale in the problem. The radiative cooling of air near ground depends on the product

$$(1 - \epsilon_g) (d\epsilon_a/dz)_{z=0}$$

which cannot be ignored even if ϵ_g is close to unity, because the multiplying derivative is huge. It must be emphasized that cooling and heating rates depend on gradients, and that near ground the gradient of the emissivity of air may overwhelm that of the temperature: differential absorption is therefore the key to understanding why the air cools down so much.

The value of the ground emissivity depends very much on the nature of the surface, and (in spite of meteorological practice!) can often be rather less than unity. A table compiled by Paltridge and Platt²⁹ shows that for some surfaces ϵ_g may be lower than 0.8. Indeed these authors point out that the common meteorological assumption $\epsilon_g = 1$ can pose problems that are not minor. Furthermore, the values listed in such tables usually refer to vertical emissivities appropriate to remote measurement of temperature by vertically oriented radiometers on spacecraft. The quantity relevant in our discussions is the global or hemispherical emissivity, which for natural surfaces may be rather less because of radiation incident at low angles. It is therefore reasonable to assume that the global emissivities of natural surfaces are in the range of 0.8 to nearly 1.0. (There is some resistance among meteorologists to the idea of surface emissivities less than unity, in part because the implications for climate are seen as profound. While these implications demand close investigation, it is useful to remember that about 71% of the earth's surface is water, and another 3-4% is ice or snow, all of which are radiatively almost black; so the envisaged revision in emissivity over the earth's surface as a whole will be no more than a few per cent, but even such apparently small changes could well have significant effects.)

By the way it is interesting to note that the standard screen height, that is the height at which the thermometers are mounted within the familiar white screen of a meteorological station, is usually just above the emissivity sublayer. Whether by design or accident, or as a result of hard experience, this height is just enough to ensure that in general temperature readings are not strongly influenced by the vagaries of the ground surface, but this is a question which, once again, calls for further investigation.

The second parameter in the model we have proposed, namely soil conductivity, is important because it determines how fast the ground cools; higher the conductivity lower is the cooling rate, because of greater upwelling heat flux from warm soil underground. Raschke realized the importance of this parameter.

The gist of the proposed theory can now be simply stated⁵. When ground is not perfectly black air above ground can cool radiatively because of the rapid variation (with height) of the absorption of infrared radiation by water vapour. Because of long photon mean free paths (especially in the so-called atmospheric window, wavelength 8-14 μ) a radiative slip at ground will usually be present. The sign of this slip can be such that the ground is warmer if the soil is sufficiently conducting to keep ground cooling slow. A touch of diffusion, chiefly only molecular, smears out the slip into the cold layer observed by Ramdas.

All of these effects, including the coupling between heat fluxes in the air with that in the soil due to thermal conduction, have been incorporated into our detailed mathematical model¹; comparisons with observations are shown in Figures 6 and 7, and are about as good as can be expected in this kind of study.

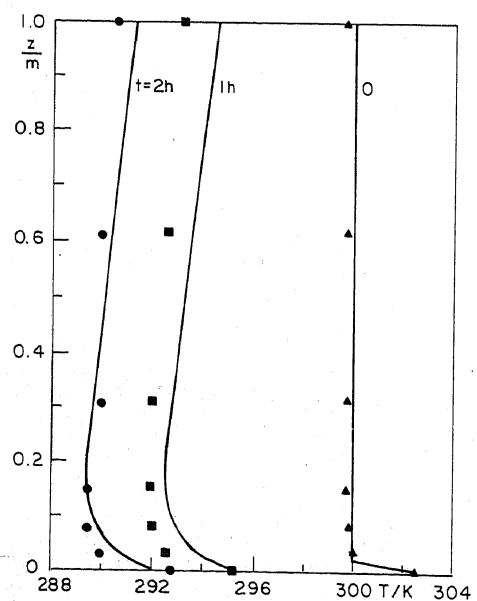


Figure 6. Comparison of observed temperature profiles showing a lifted minimum with predictions from theoretical model.

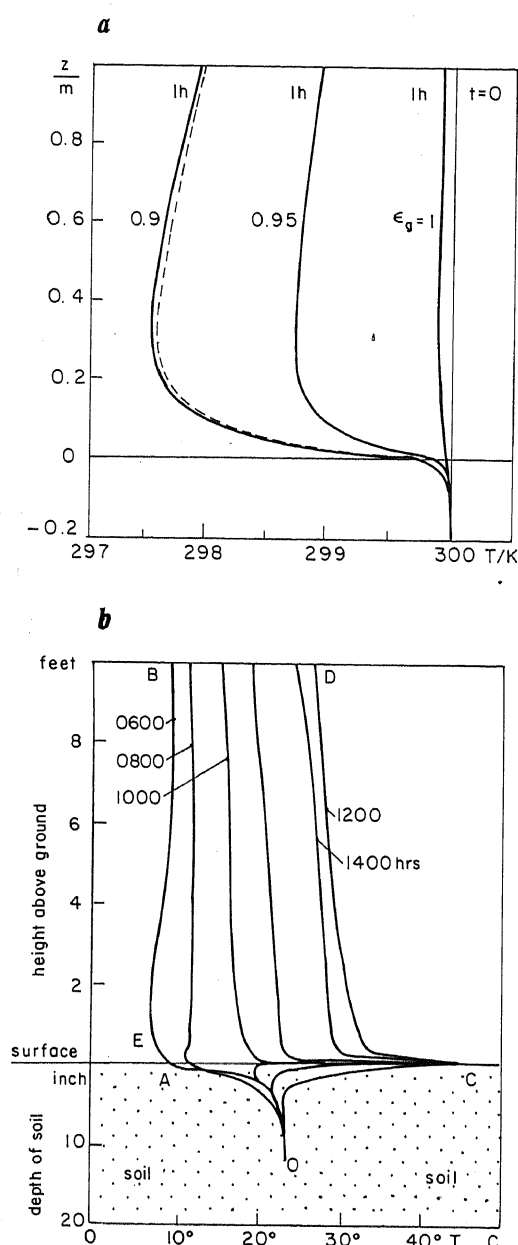


Figure 7. Temperature profiles in air and soil, as computed by a theoretical model¹ (a), one hour after sunset, at different values of ground emissivity ϵ_g , compared with measurement¹⁵ (b): note that the comparison can only be qualitative (the two figures are also drawn to different scales), as the values of model parameters for the measurement site are not known. The full lines in (a) are obtained from use of an approximate boundary condition at ground, and the dashed line from a complete air-soil coupled model.

What our model shows is that the energy balance in the air layers near ground is extremely delicate³⁰. It is for this reason that radiative transfer calculations have to be very carefully made. Earlier theoretical attempts were not robust (and hence not decisive), as they led to conclusions that would be altered if the underlying assumptions were modified even slightly. It is only in

the last two decades that atmospheric radiation has come to be treated with some confidence³¹, thanks to the development of computer codes that carry out line-by-line integration across the absorption spectrum in the atmosphere, and the gradual improvement of the so-called flux-emissivity scheme, which is what we have used in our model.

There remains the question of how the Rayleigh-Benard instability is circumvented. This must be an effect of radiation, for it is easy to see that radiation is stabilizing. For a given temperature difference the presence of radiation adds to the heat transfer by conduction and so may be thought of as increasing the effective conductivity of the medium. This becomes literally true when the medium is nearly opaque, for then a radiative thermal diffusivity K_r can be formally introduced. The viscosity of air is of course not affected by radiation, so momentum diffusion is much less than thermal diffusion, i.e. air behaves in this limit like a low Prandtl number fluid. Now it is well known that the critical Rayleigh number for onset of convection is unaffected by Prandtl number. It is therefore reasonable to expect that a modified Rayleigh number, with $K_r + K_m$ replacing the molecular diffusivity K_m , would have the same critical value for instability as in the non-radiative situation, everything else remaining the same. The classical Rayleigh number (defined with only the molecular thermal diffusivity K_m in the denominator) will therefore have, with radiative diffusion, a critical value that is larger by a factor of order $(1 + K_r/K_m)$. This factor can be considerable, so the critical Rayleigh number can go up substantially. When the medium is optically thin the argument is not literally valid, but the additional transfer of heat by radiation should even then have the qualitative effect of stabilizing the flow. A rigorous assessment of the effect of radiation with the semi-open boundary conditions characteristic of the atmospheric problem is still to be carried out, but estimates made by us¹ (based on arguments involving the ratio of radiative to diffusive time constants) show that the critical Rayleigh number under conditions of interest can go up by a factor that is anywhere between 10 and 150. Thus the Ramdas layer is not as unstable as it seems at first sight: and indeed (in the absence of winds) it often sustains itself from sunset to sunrise. Furthermore, heat transport by free convection increases only slowly at supercritical Rayleigh numbers: for it to reach four times the conductive flux the Rayleigh number has to be about 60 times larger than critical. We thus see that the lifted minimum can be maintained without completely over-turning either solely due to radiative stabilization or because heat transport is only weakly enhanced even at relatively large super-critical Rayleigh numbers: the heavier fluid is prevented from sinking because viscosity aided by radiation holds it aloft, so to speak.

The present theory predicts that the lifted minimum is weaker on rough, dark (radiatively, that is) and insulating ground, and disappears if turbulent transport exceeds some four times the molecular transport. These predictions lend themselves to experimental checks, which therefore now become interesting to carry out.

There is some irony in this story, for the Poona data in the very first report of Ramdas and Atmanathan are almost certainly contaminated by advection, as the authors themselves suspected. Neither the height nor the intensity of this first study of the lifted minimum, both substantially at variance with all later reports (including those of Ramdas himself), can be reproduced by the present theory for any reasonable values of the model parameters. But that first finding triggered a host of remarkable investigations here and abroad. It is interesting to reflect that there is so much that is intriguing in the lowest metre of the atmosphere—in the layer which we explore with our feet all the time—and that we take longer to understand its dynamics than that of the far reaches of the atmosphere that are so difficult to access.

But one can ask at this stage whether the problem is worth all this attention: does it matter very much if the temperature is a few degrees this way or that just above ground? Apart from the intrinsic scientific interest of the problem itself, the temperature field near the ground is important in determining the environment in which crops grow—this has in fact been the major motivation for the investigations we have reviewed here. A lifted minimum could have implications in agriculture and horticulture: there are reports of how in tomato plants frost first affects fruit well above ground, if the soil is bare¹⁰. Surely there must be conditions when retrieval of surface temperatures by remote sensing techniques would have to account for near-surface phenomena and parameters more adequately than it does now: after all, meteorologists want sea surface temperatures to a fraction of a degree. But beyond all this we must realize that an understanding of the singular phenomena in any field advances the state of the art in the field as a whole. Perhaps the present study will help introduce quantitative mathematical models for what has otherwise remained a largely empirical science: one may look forward to opening up what may legitimately be called theoretical 'sub-micro' meteorology, and to the emergence of computer models that can predict weather and climate in the lowest metre of the atmosphere.

Finally, it is an opportunity to pay tribute to a true pioneer: Ramdas (—with his coworkers: let us not forget Atmanathan, who died young in rather tragic circumstances) showed how to bring deep scientific insights and a fresh and original viewpoint to the study of (literally) down-to-earth problems, with an unerring instinct for the significant that was not recognized by the fashions of the time.

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The chemistry of Fischer carbene complexes: Discovery of a new rearrangement reaction*

Kashinath M. Sathe, Malay Nandi and Amitabha Sarkar

Fischer carbene complexes have emerged as an important organometallic intermediate for the synthesis of a wide variety of target organic molecules. The reactivities of these complexes do not always follow a predictable pattern. An unprecedented rearrangement of these complexes discussed herein is triggered by an apparently minor structural variation.

Background

SINCE their discovery by E. O. Fischer in 1964, the rich and varied chemistry of Fischer carbene complexes has been extensively explored¹. This led to their utilization as useful intermediates for the synthesis of numerous complex carbocyclic and heterocyclic molecules of biological interest.

The reactivity pattern of the Fischer carbene complexes can be rationalized in terms of its structure (Figure 1). The octahedral complex contains five carbon monoxide ligands around the metal. The sixth ligand is a substituted alkoxymethylene group, where bonding to the metal occurs via the non-bonding electron pair on the methylene carbon. Five strong π -acceptor CO ligands deplete the electron density on the metal and consequently the methylene carbon is rendered electrophilic. This centre is, therefore, susceptible to nucleophilic attack. As a result of electrophilicity of the carbene carbon, on the other hand, the proton on the α -carbon is rendered acidic ($pK_a > 8$), and carbanion chemistry becomes accessible. In addition, the $M(CO)_5$ fragment can undergo ligand substitution and open up other reaction pathways.

The characteristic spectral features of Fischer carbene complexes are also consistent with its structure and symmetry. For instance, except for the CO group *trans* to the carbene ligand, four other CO ligands are equivalent by symmetry. Thus, the CO stretch in IR spectrum displays two distinct peaks at 2050 (s) and 1970 (vs) cm^{-1} , while the ^{13}C NMR spectrum displays two signals in the range 200 to 230 ppm in the ratio 1:4. The electrophilic carbene carbon signal appears at 340 to

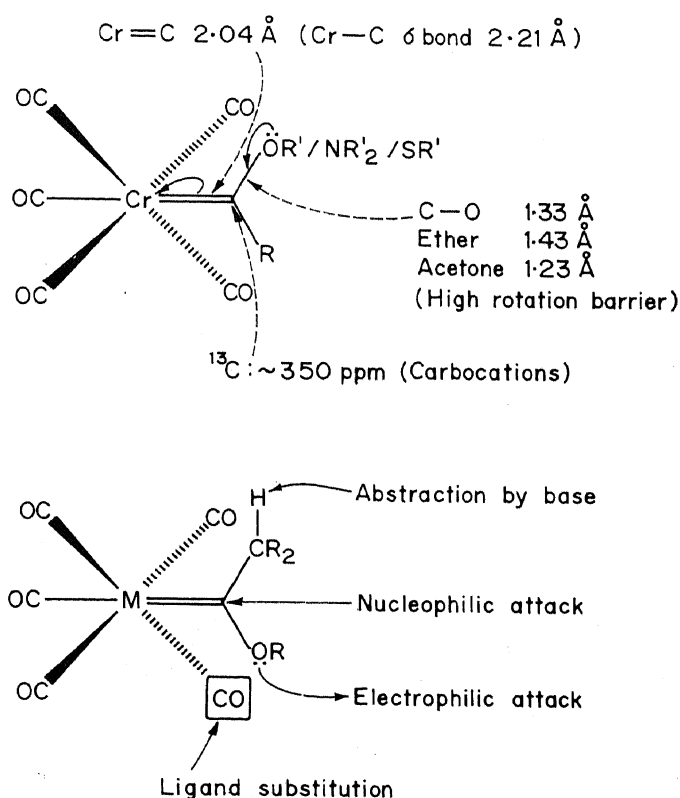


Figure 1.

360 ppm. Such diagnostic spectral features are extremely useful for straightforward identification of these complexes.

An interesting stereochemical feature of $(CO)_5M = C(OR)(Ar)$ complexes is that the aryl ring is oriented orthogonal (*out of conjugation!*) to the metal-carbene π -plane in the solid state, as shown by X-ray crystallography. Such preference may be countered to an extent

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by electron-releasing OR or NR₂ group in the *para* position. Such orientation is not imposed by crystal packing forces. We have now obtained clear ¹H NMR evidence that the orthogonal orientation of the aryl ring can be attained at a low enough temperature in solution. For example, in the low temperature spectrum shown in Figure 2, two sets of benzyl signals are observed for the carbene complex. The broad singlet appears close to the normal position. The doublet of doublet is shielded considerably by the aromatic ring anisotropy. Since the aromatic ring is unsymmetrically substituted, the two benzyl protons are rendered non-equivalent.

Among the several synthetically useful reactions of Fischer carbene complexes, the benzannulation reaction discovered by Dotz^{1c} is the most exploited. An aryl, heteroaryl or alkenyl chromium alkoxy-carbene complex reacts with acetylenes under thermal conditions to generate a new aromatic ring as shown in Scheme 1. This reaction has been applied to the synthesis of several biologically important molecules such as Daunomycinone, Deoxyfrenolicin, Nanaomycin, Khellin, Sphondin,

Thiosphondin, Vitamin E and several compounds in Vitamin K series (Chart 1).

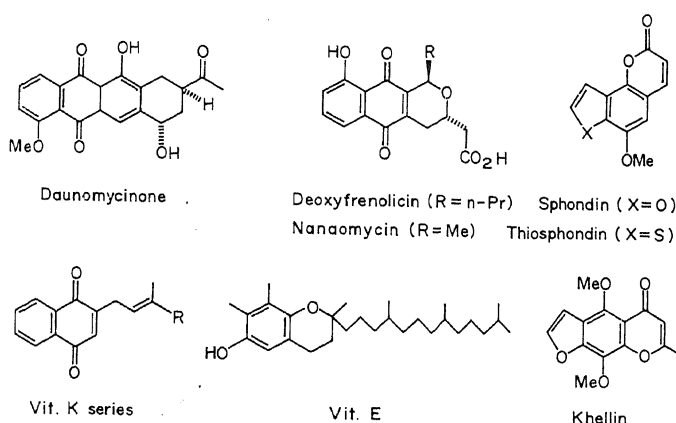


Chart 1.

Diels-Alder reactions of α,β -unsaturated alkoxy-carbene complexes with dienes proceed with much greater facility than observed with corresponding esters (Scheme 2), reminiscent of Lewis acid catalysis in such reactions.

Under photochemical conditions, Fischer carbene complexes of chromium react with Schiff bases to afford β -lactams² (Scheme 3). The reaction is believed to

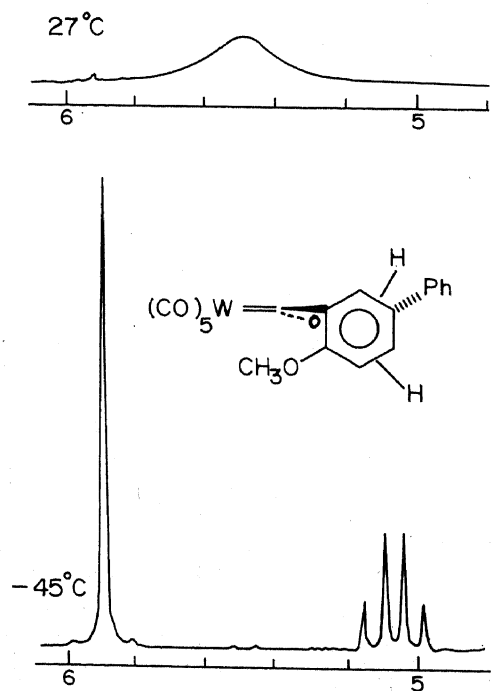
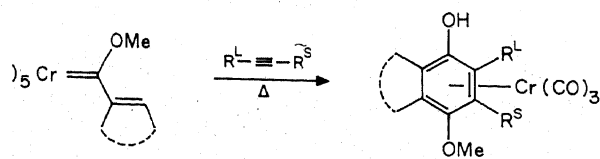
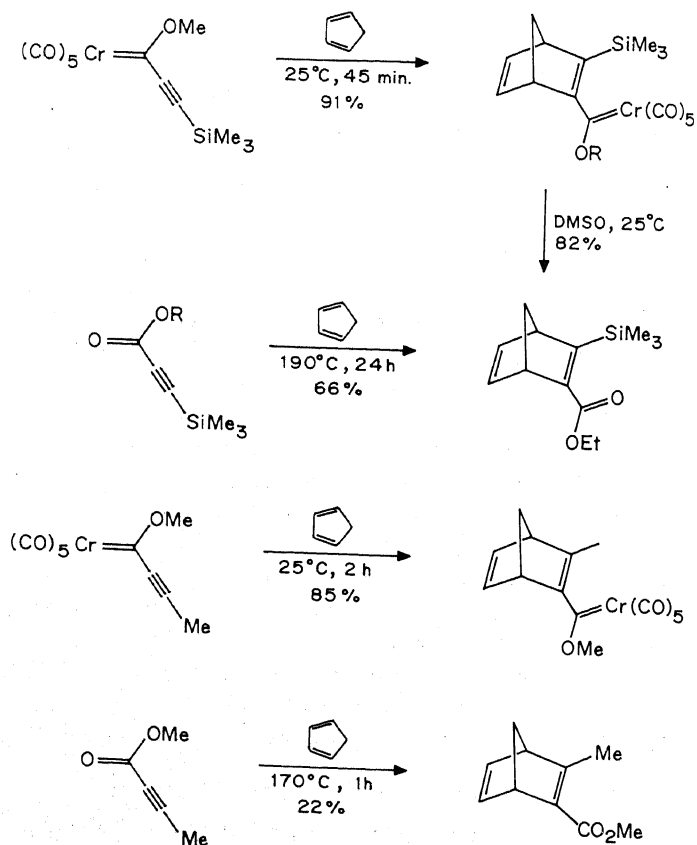


Figure 2.

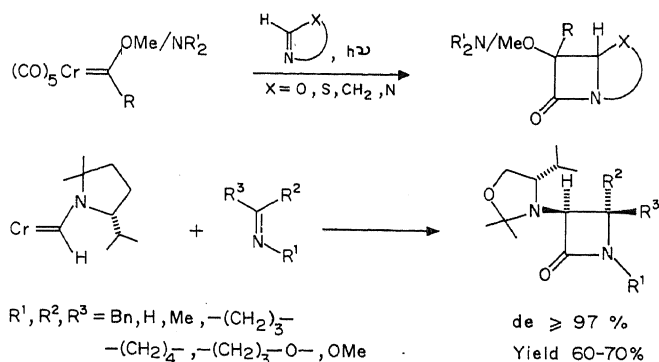


Dotz reaction

Scheme 1.



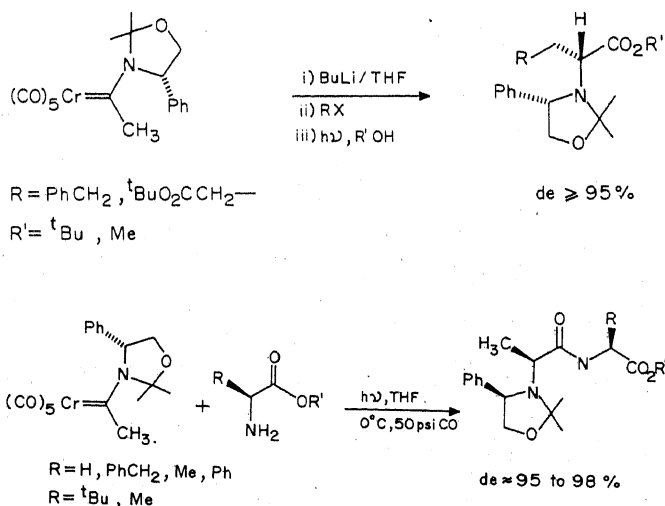
Scheme 2.



Scheme 3.

proceed *via* a ketene complex which undergoes [2 + 2] cycloaddition with the Schiff base. Excellent stereocontrol has been achieved in this reaction, and it has been possible to synthesize a variety of optically active β -lactams by this method. When the reaction is carried out under CO pressure, $\text{Cr}(\text{CO})_6$ precipitates out of the reaction mixture and it can be recycled.

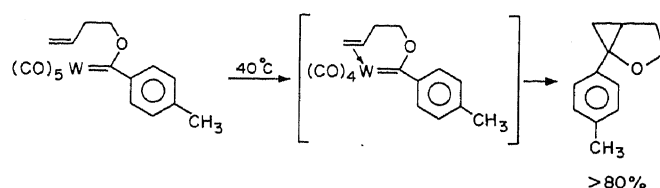
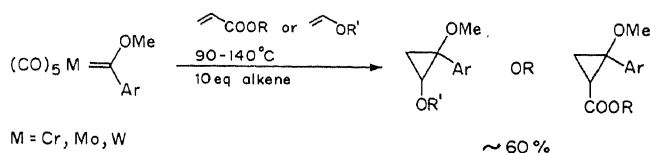
Alternatively, the metal-ketene complex can be solvolyzed *in situ* to obtain N-protected amino acid or esters³ (Scheme 4). The extent of chiral induction was high with carbene complexes derived from chiral amines. Recently dipeptides have been synthesized with high diastereoselectivity using this method.



Scheme 4.

Much of the early work was directed towards release of the carbene ligand and observation of reactions typical of free carbenes, e.g. cyclopropanation. Reaction with

a number of alkenes revealed that activated olefins (electron-rich or electron-deficient) provided cyclopropanes on heating at temperatures greater than 90°C although intramolecular cyclopropanations are much more facile and requires no such activation (Scheme 5).



Scheme 5.

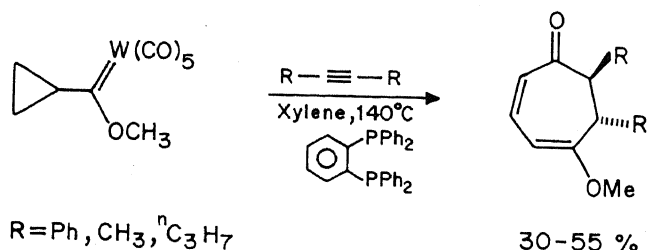
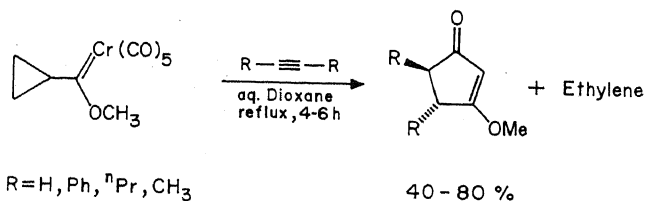
There has been an increasing trend in recent years to explore new reaction pathways in the chemistry of Fischer carbene complexes, by making structural changes in the carbene ligand. For example, it has been shown that the reactions of an acylmetallate salt with alkynes result in the formation of butenolides in good yields (Scheme 6) while benzannulation is not observed⁴.



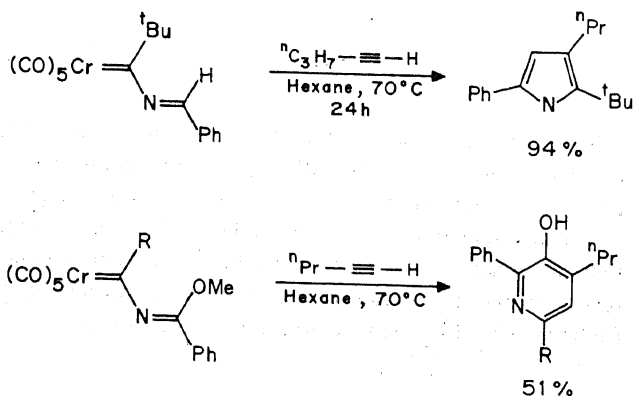
Scheme 6.

Cyclopropyl methoxycarbene complex of chromium reacts with alkynes to afford cyclopentenones. But the corresponding tungsten complex reacts with alkynes *via* a different pathway to provide cycloheptadienones⁵ (Scheme 7).

With appropriately substituted carbene derivatives one can devise useful reactions to obtain heterocycles⁶ (Scheme 8).



Scheme 7.

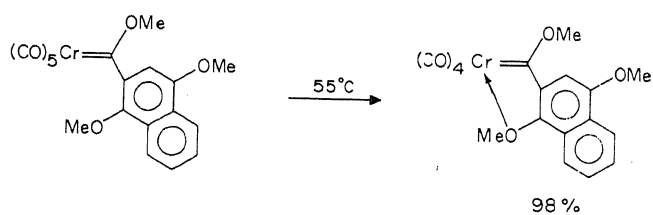


Scheme 8.

In our work, we discovered a new pathway in thermolysis of Fischer carbene complexes caused by an apparently minor variation in the oxygen substituent.

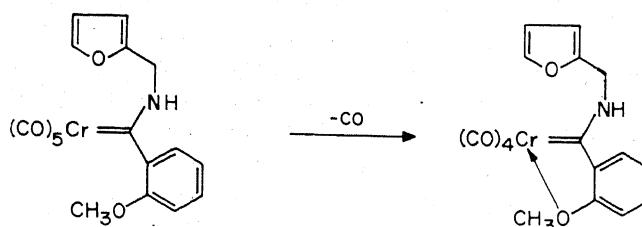
Present work

Although Dotz reaction has found extensive use in organic synthesis, the reaction is successful only with chromium carbene complexes. The tungsten carbene complexes, which are generally stable crystalline solids, lend themselves to easier manipulation but do not undergo benzannulation reaction. The higher W-CO bond strength retards both the initial decarbonylation to create a vacant coordination site and the CO insertion necessary at a later stage. Intramolecular chelation was shown to accelerate dissociation of a CO ligand in the case of chromium and tungsten carbene complexes (Scheme 9). We thought it would be desirable to have a weakly coordinating group which could intramolecularly stabilize



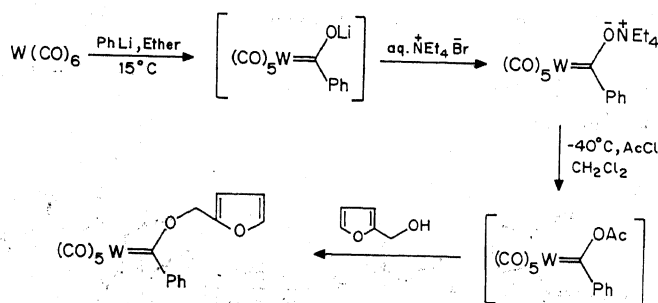
Scheme 9.

the CO by chelation, but would not compete with incoming ligands for coordination with the metal. From a report by Dotz in 1987 which showed (Scheme 10) that a methoxy group preferentially complexed with the metal than the competing furan moiety, it appeared that furan as a poor donor might meet the above criteria.



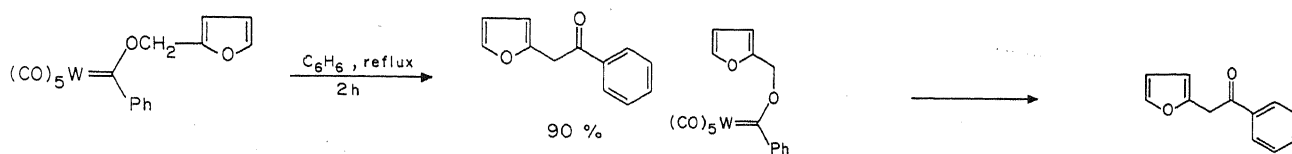
Scheme 10.

The phenyl furfuryloxy carbene complex of tungsten was prepared by the conventional route (Scheme 11) and purified by column chromatography to furnish a red, crystalline, moderately air-stable solid.



Scheme 11.

Thermolysis of this complex in benzene produced a complete surprise. The starting material was consumed and no new carbene complex was obtained. The only product isolated after chromatography was a ketone as shown in Scheme 12, in 90% yield. The ketone was derived from an unprecedented rearrangement of the carbene complex!



Scheme 12.

Preliminary experiments quickly identified at least two essential structural criteria that must be met for the rearrangement to occur: the oxygen must be connected to a benzylic centre, and, an aromatic ring must be attached to the carbene carbon. The results are summarized⁷ in Table 1.

The rearrangement of the free carbene derived from the organic ligand could lead, in principle, to the same product. This possibility was discounted on the ground that generation of free carbene from a Fischer carbene complex has never been observed before. A few experiments were carried out to unravel the salient mechanistic features of this reaction.

Photolysis of the carbene complex **1c** in benzene at room temperature afforded the ketone in 60% yield suggesting that initial CO decomposition is probably the rate-determining step. This is further supported by the observation that furfuryloxy carbene complexes underwent rearrangement in refluxing benzene while other benzyloxy complexes reacted better in refluxing toluene.

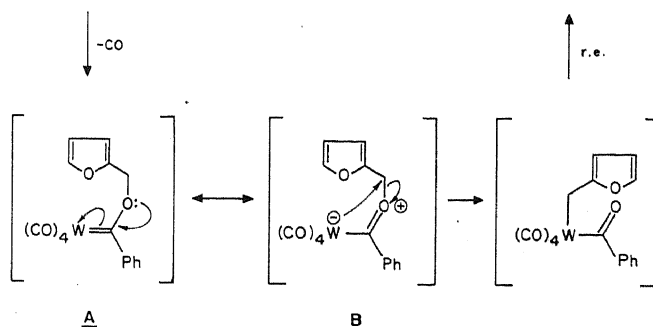
The *p*-methoxybenzyloxy carbene complex **1b** reacted faster (16 h in benzene) than the benzyloxy carbene complex **1a** (> 44 h in benzene) indicating the importance of stabilizing an incipient carbonium ion adjacent to the oxygen. Also, a *p*-OMe substituent on the aromatic ring connected to the carbene carbon (as in **1e**) appeared to impair the efficiency of the reaction.

A mechanistic scheme was proposed (Scheme 13), which accommodated these observations. Initial CO loss from the carbene complex generates a 16e intermediate **A**. The electronic polarization of **A** generates **B**, which undergoes cleavage of the carbon-oxygen bond to produce an acylmetal intermediate. This furnishes the product ketone by a facile reductive elimination.

The structurally similar Fischer carbene complexes of chromium also underwent such thermal rearrangement to afford arene-chromium complexes (Table 2). The

Table 1. $(\text{CO})_5\text{W}=\text{C}(\text{R})(\text{OCH}_2\text{Ar}) \xrightarrow{\Delta} \text{R}-\text{CO}-\text{CH}_2\text{Ar}$

No.	R	Ar	Solvent	Time (h)	Yield (%)
1a	Ph	Ph	Toluene	2	56
1b	Ph	<i>p</i> -OMe-C ₆ H ₄	Benzene	16	56
1c	Ph	2-Furyl	"	2	90
1d	<i>p</i> -Me-C ₆ H ₄	"	"	3.5	65
1e	<i>p</i> -OMe-C ₆ H ₄	"	"	10	36
1f	<i>p</i> -OMe-C ₆ H ₄	"	Toluene	1.5	50
1g	Me	"	Benzene	3	-



Scheme 13.

yields were moderate to good, partial decomplexation being unavoidable under the present reaction condition. The Cr(CO)₃ fragment was found to be appended to the more electron-rich aryl ring exclusively.

The diastereoselectivity of this rearrangement could be probed by the use of *o*-methoxyphenethyl alkoxy group. The product would have two chiral centres: one at the benzyl carbon and the other due to the metal complexation to an unsymmetrical aromatic ring. The carbene complex **2d** provided a single diastereomer of the product complex on heating at 80°. No diastereomeric mixture could be detected by 200 MHz ¹H NMR or analytical HPLC with UV detector. Such high diastereoselectivity is suggestive of a high degree of organization in the transition state. The diastereoselectivity was lower if the bath temperature was raised (> 90°). Epimerization of the product could be effected by base. It was established that the diastereomer obtained in the rearrangement was the kinetic product. The structure of this complex was confirmed by X-ray diffraction (Figure 3).

However, further experiments revealed that diastereoselectivity in the reaction is probably of steric origin. The *o*-methyl phenethyl alkoxy carbene proved to be less

Table 2. $(\text{CO})_5\text{Cr}=\text{C}(\text{R})(\text{OCHR}^1-\text{Ar}) \xrightarrow[\text{Benzene}]{\Delta} (\text{CO})_3\text{Cr}-\text{Ar}-\text{CHR}^1-\text{CO}-\text{R}$

No.	Ar	R	R ¹	Yield* (%)
2a	Ph	Ph	H	68
2b	<i>p</i> -OMe-C ₆ H ₄	Ph	H	77
2c	Ph	Ph	Me	43
2d	<i>o</i> -OMe-C ₆ H ₄	Ph	Me	47
2e	<i>o</i> -OMe-C ₆ H ₄	Ph	H	48
2f	Ph	Me	H	-

*Total yield of decomplexed ketone is about 15–20% higher in all cases.

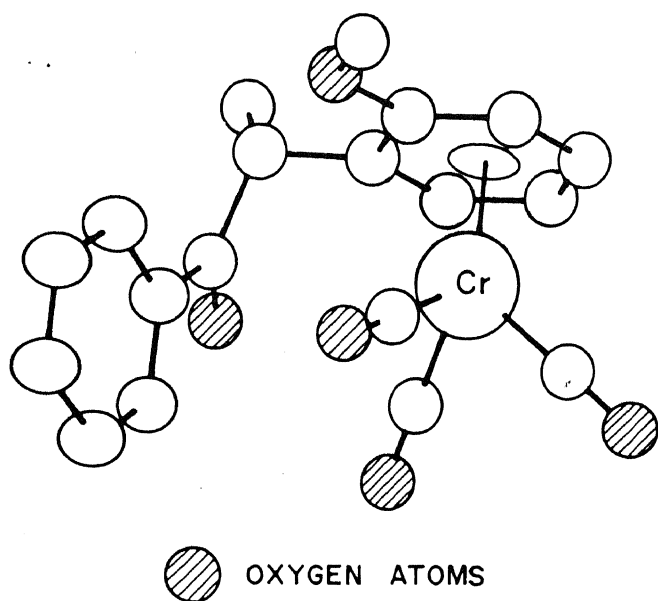


Figure 3.

diastereoselective and *m*-substituted benzyloxy carbene complexes were not selective at all.

In summary, we have described an unusual rearrangement reaction of arylmethoxy aryl carbene complexes of tungsten and chromium, which was observed as a

fortunate accident. But this also reminds us of the complexity of diverse reactivity patterns such organometallic compounds display, in order to challenge the wits of practising chemists.

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Synthesis and properties of novel π -electron donors—Variants of tetrathiafulvalene*[†]

M. V. Lakshminantham and Michael P. Cava

The remarkable one-dimensional conductivity exhibited by the charge transfer complex formed from tetrathiafulvalene (TTF) and tetracyanoquinodimethane has sparked attempts to synthesize related organic metals. In particular, the possibility of utilizing alternative π -donors has attracted considerable attention. In this article, the synthesis and electrochemical characterization of a number of TTF analogues with different olefinic and heterocyclic spacer groups are described.

ORGANIC synthesis continues to play an increasingly important role in modern technology as we approach the twenty-first century. Almost everyone is familiar with liquid crystal displays in electronic equipment, watches and novelty devices. It is anticipated that organic

synthesis will lead to synthetic materials with metallic properties, conductors, superconductors, ferromagnets, NLO materials, photoconductors, etc. Synthetic metals are bound to find applications in electronics, plastic batteries etc. Photoconductors, semiconductors and superconductors have applications in photocopiers, solar cells, computer logic gates, etc.¹.

The focus of this article is limited to the synthesis and properties of compounds which may be important in the design of organic conductors or superconductors.

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*Dedicated to Prof. T. R. Govindachari on his 77th birthday.

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