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Jet-Cooled Exciplexes. 4. Diethyl Ether and Anisole with Anthracene, Perylene, and Methyl-Substituted Anthracenes

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Abstract: Fluorescence from pairs formed in a supersonic expansion of a mixture of anthracene or perylene with diethyl ether (DEE) or anisole in helium is observed under UV laser excitation. Complexes formed with anthracene exhibit two different types of fluorescence. One consists of broad excitation and emission bands and exhibits long decay times—it is attributed to exciplex formation. The other shows structured bands and short decay times and is attributed to excited van der Waals (vdW) complexes. Perylene complexes emit only vdW fluorescence. Substitution of the 9,10-positions in anthracene with methyl groups results in the appearance of structured excitation and emission bands with a relatively long decay time, while a substitution of the 2-position leads to only minor changes in the fluorescence characteristics. These results are compared to similar experiments by using amines instead of ethers and are interpreted in terms of an orbital orientation model involving localized electron transfer.

Exciplexes are considered as important intermediates in many photochemical reactions.[1] Their properties are most conveniently deduced from characteristic emission spectra. In some cases, however, their existence is inferred from mechanistic or kinetic considerations, even though no direct observation (for instance, by fluorescence spectroscopy) is available. The absence of fluorescence in these cases has been sometimes ascribed[2] to low quantum yields, caused by rapid radiationless processes. In fact, it has been suggested that in cases where the exciplex leads efficiently to reaction, its fluorescence yield would be expected to be small.

Supersonic jet expansion[3] provides, in principle, a means to reduce the efficiency of some of the radiationless processes. In this method, one forms adducts between the would be exciplex components by seeding them in a high pressure inert carrier gas and expanding the mixture through an appropriate nozzle into high vacuum. Adduct formation is accompanied by extensive cooling, so that most internal degrees of freedom are essentially frozen. Furthermore, downstream from the nozzle, collisions between the adduct and other molecules are very rare, so that both intramolecular and intermolecular quenching processes are slowed down considerably.

Thus, in a supersonic expansion one may observe emission from electronic excited states that are otherwise so weakly fluorescent that for all practical purposes they may be termed "dark" states. Indeed, several reports of exciplex emission in supersonic jets have appeared in the last few years.[4-8] Some of these systems, for instance, anthracene–ammonia,[7] have not yet been observed to exhibit exciplex emission in the bulk.

The assignment of a given emission band as due to an exciplex is helped, in bulk liquid solution, by considering the properties of the solvent.[9] Thus it has been shown that the quantum yield of exciplex emission often decreases as the solvent polarity increases, due to ionic dissociation. In the jet, one deals with collision free species, that undergo no interaction with a solvent. The characterization of a given species as an exciplex must thus rely only on properties of the adduct itself. Another major difference between solution and jet-cooled exciplex is in the formation mechanism. In both cases the exciplex is formed from an electron acceptor A and electron donor D. In the bulk the interaction between the donor and the acceptor before optical excitation is negligible. Photon absorption can thus be envisioned as occurring in only one of them, for instance, the acceptor. The exciplex is formed following a collision between the electronically excited acceptor, A^*, and the donor, to form a collision complex $(A^*D)_{solv}$ which quickly transforms to an exciplex, A^-D^+, in which complete or partial electron transfer has taken place.

In the jet the pair is formed, as a van der Waals adduct, before light absorption takes place. Electronically excited van der Waals adducts may be considered as locally excited states of one of the constituents (without loss of generality, assume again that it is the acceptor), which is attached to the other and denoted as A^*D. The fluorescence excitation and emission spectra of van der Waals adducts have been studied extensively in the last 10 years.[10-12] They usually consist of a series of discrete vibrational bands that are red-shifted with respect to the transitions of the bare molecules. Both excitation and emission bands are narrow, usually limited by the optical resolution and by the fact that several rotational states are populated, leading to a rotational envelope which is 1-2-cm^{-1} wide.

The model proposed for exciplex formation in jet-cooled adducts[5,6] calls for an interaction between the locally excited (LE) state and the charge-transfer (CT) state. A typical energy level diagram is shown in Figure 1. (A more detailed discussion may be found elsewhere.[5,6,13]) Excitation may be directly to the CT state, whereupon a very broad excitation band is expected. However, in many cases several distinct bands are observed in excitation, much broader than the previously van der Waals type (widths up to 300 cm^{-1} have been reported), but still much narrower than expected for direct transitions to the CT state. (In an example for the latter,[14] the tetracyanoethylene–paraxylene system, a width of $\sim$3500 cm^{-1} was reported).

The observed excitation spectrum was accounted for by assuming initial excitation of the locally excited state, which is coupled to the CT one. The discrete nature of the spectrum is due to Franck–Condon transitions into discrete vibrational levels of the LE state. The rate of transition between the two excited states can be expressed by Fermi's golden rule

$$P = (2\pi/h)V^2_{\text{LE,CT}}\rho \qquad (1)$$

where $V_{\text{LE,CT}}$ is the electronic coupling matrix element between

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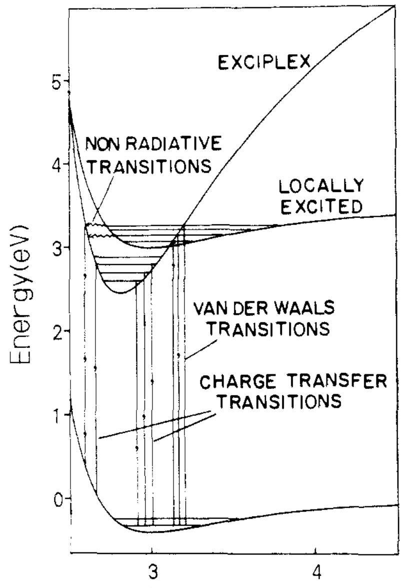

Figure 1. A schematic representation of the energy level diagram of an adduct capable of forming an exciplex. R is the separation between the two components. The ground state and the locally excited state are stabilized typically by 0.1–0.3 eV, while the exciplex state is stabilized by 3–5 eV. Optical absorption from the ground state leads preferentially to the locally excited state, if a direct transition to the exciplex state is forbidden by a selection rule. Nonradiative transition can then lead to population of the exciplex. The emission spectrum of the exciplex is usually broad and structureless, since Franck–Condon transitions are largely to the repulsive part of the ground-state surface. Some structures may appear toward the blue edge of the spectrum, due to bound–bound transitions.

the two states. In the Born–Oppenheimer approximation it may be written as

$$V_{\text{LE,CT}} = \langle \phi_{\text{CT}}|V|\phi_{\text{LE}}\rangle\langle \chi_{\text{CT}}|\chi_{\text{LE}}\rangle \qquad (2)$$

where the total wave function, ψ, is expressed as the product $\psi = \phi\cdot\chi$ of an electronic and nuclear motion wave function, ϕ and χ, respectively. The symbol ρ in eq 1 represents the density of states of the CT state.

The emission spectrum of exciplex systems consists, even in the jet, of broad and unstructured bands, since it is dominated by transitions from the bound CT state to the repulsive part of the ground-state potential (cf. Figure 1). Some structures may appear in the *blue* end of the spectrum. Since solvent dependent parameters such as solvent shifts, polarity dependence of the fluorescence yield, etc., cannot be used to help in assigning jet spectra, the form of the emission spectrum is of crucial importance in characterizing jet-cooled exciplexes: indeed, it is well known that van der Waals bound LE states display a discrete emission spectrum.[10-12] Another aid in identifying an exciplex is the fact that decay times are often much longer than for the corresponding LE states.[5-8]

In this paper we report the observation and characterization of jet-cooled exciplexes of ethers. Some aromatic ethers, such as anisole and methyl naphthol, have been reported to form exciplexes[15,16] in fluid solutions at room temperature, while no such reports were made on aliphatic ethers. It turns out that some aliphatic ethers, such as diethyl ether, may also form fluorescent exciplexes with anthracene and some of its derivatives. In contrast, no exciplex emission is obtained, under identical experimental conditions, from an adduct of anthracene and tetrahydrofuran. It has also been found that substitution of the hydrogen atom in the 9- or 10-position of anthracene can effectively prevent exciplex formation. These results are discussed in terms of the electron-transfer model previously suggested for the amine–anthracene systems.[5,6,13]

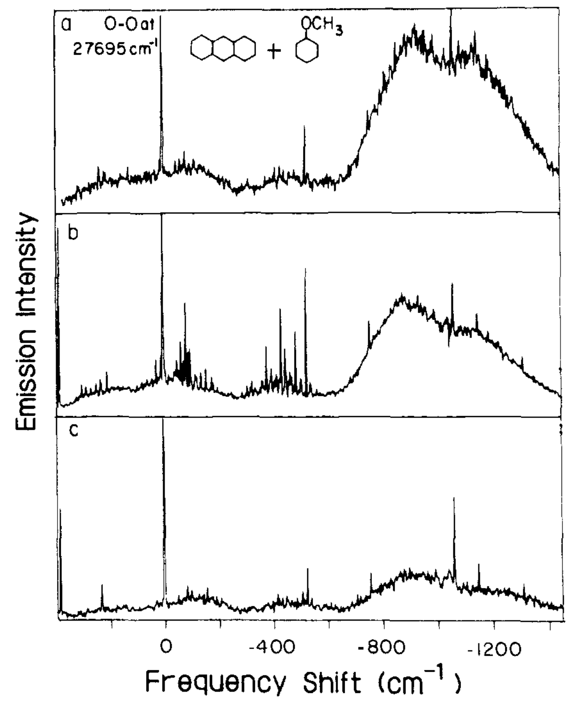

Figure 2. Excitation spectra of anthracene–anisole adducts in a helium jet. Anthracene crystals were held at 100 °C, observation is at 470 nm. (a) Spectrum taken with 1 Torr anisole at a time interval 40–60 ns after the laser pulse. (b) Same as (a) at a time interval 0–20 ns after excitation. (c) Same as (a) with anisole pressure 0.3 Torr.

Experimental Section

The experimental setup was described in detail[6-8] earlier, so that only salient features and changes will be described. The ether vapor was mixed with helium (0.02–0.1% v/v), and the mixture was allowed to pass over heated crystals of the hydrocarbon. The temperature of the crystals was controlled to +1 °C, allowing accurate determination of the vapor pressure, which was usually maintained between 0.1 and 1 Torr. The resultant mixture, held at an overall pressure of 3–6 atm, was allowed to expand through a magnetically activated 0.35-mm nozzle, operated at 10 Hz, into a chamber pumped to a vacuum of 10^{-5} Torr. The resulting molecular beam was crossed by a dye laser beam 30–50 nozzle diameters downstream. Two different pulsed laser systems were used: a nitrogen laser pumped dye laser (1-cm^{-1} bandwidth, 7-ns pulsewidth), described before,[6] and a newly acquired excimer laser pumped dye laser (Lambda Physik's FL3001 pumped by EMG101 MSC XeCl laser, bandwidth 0.2 cm^{-1}, pulsewidth 17 ns). Fluorescence was collected at right angles to both molecular and laser beam, imaged on the entrance slit of a 1/4 m monochromator (Bausch & Lomb) and detected by a fast photomultiplier (Hamamatsu R1332). The signal was digitized at 150-MHz bandwidth (Tektronics 2430) and averaged by a personal computer. The whole decay profile was recorded for each shot, and time resolved spectra could be obtained by displaying appropriate "time windows" across the profile. Typical spectra were obtained by averaging 30–200 shots.

Perylene, anthracene, and substituted anthracenes were obtained from the Aldrich Company with a purity of 98–99+% and used without further purification. Anisole, tetrahydrofuran, and diethyl ether were distilled and outgassed prior to use. Samples were taken from different sources, and no impurities could be detected.

Results

Anthracene–Anisole. Typical excitation spectra obtained with this system are shown in Figure 2. Two distinct types of bands are observed: one consists of a series of relatively narrow bands (1-2 cm^{-1} fwhm) and the other of broad (fwhm > 100 cm^{-1}) and essentially structureless bands which often overlap. The two types sometimes occur in the same spectral region and thus appear as superimposed features. Emission spectra obtained upon exciting into these bands differ considerably: excitation of the narrow bands leads to structured emission similar to that observed in bare

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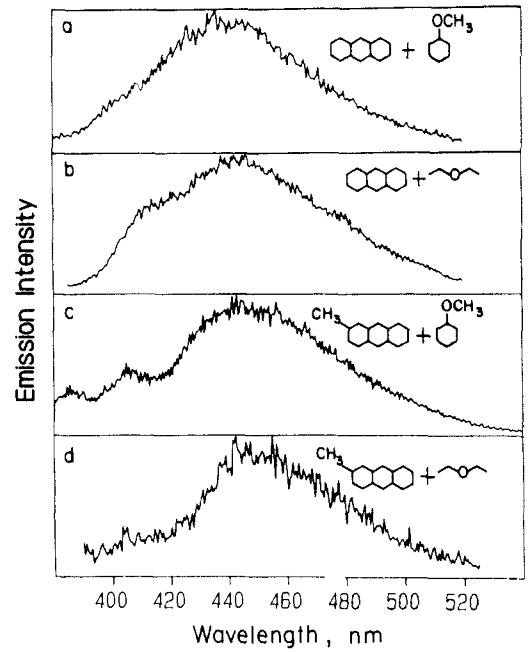

Figure 3. Emission spectra of anthracene, 2-methylanthracene adducts with ethers, obtained upon excitation of the broad bands. The spectra were recorded 20–40 ns after excitation. (a) Anthracene crystals held at 100 °C, anisole pressure 1 Torr. Excitation at 372.2 nm (−870-cm^{-1} shift). (b) Anthracene at 100 °C. DEE pressure 2 Torr. Excitation at 377 nm (−1140-cm^{-1} shift). (c) 2-Methylanthracene at 75 °C. Anisole pressure 1 Torr. Excitation at 373.2 nm (−530-cm^{-1} shift). (d) 2-Methylanthracene at 75 °C. DEE pressure 1 Torr. Excitation at 376.8 nm (−930-cm^{-1} shift).

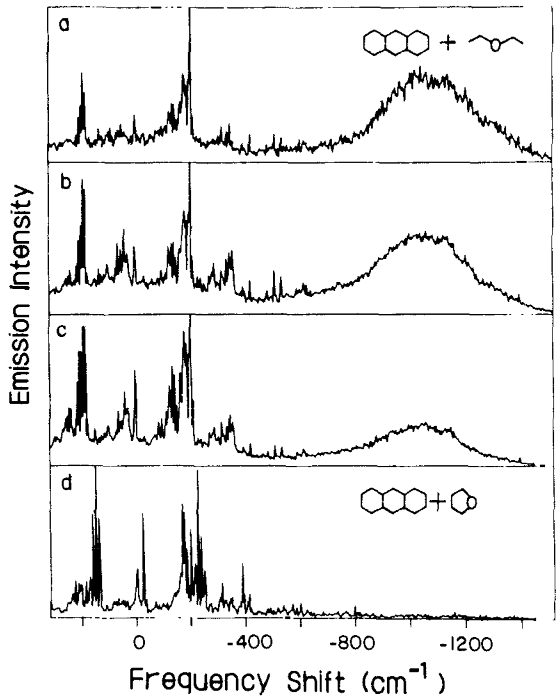

Figure 4. Excitation of spectra of anthracene–DEE adducts (top 3 panels) and anthracene–tetrahydrofuran adduct (bottom panel). Anthracene crystals were held at 90 °C, observation at 470 nm. (a) DEE pressure 2 Torr, time window 40–60 ns after excitation. (b) Same as (a), time window 0–20 ns after excitation. (c) DEE pressure 1 Torr, time window 0–20 ns after excitation. (d) tetrahydrofuran pressure 1 Torr, experimental conditions as in (c).

anthracene and slightly red-shifted with respect to the latter. Their decay time varies somewhat, depending on the choice of the excitation wavelength, between 20–25 ns (for bare anthracene 21 ns was reported[17]). This variation in decay times does not show any simple systematic dependence on the excitation wavelength. The broad excitation bands lead to a much more red-shifted emission band, peaking at 440 nm, which is unstructured. Decay times of this emission band decrease monotonically as the excitation frequency is increased across the excitation spectrum from 38 to 26 ns.

All the features displayed in Figure 2 are due to anthracene–anisole adducts, except for the 0–0 band of anthracene (used as the reference point for the shift), and the feature at −1040 cm^{-1}, to be discussed shortly. By varying the anisole pressure in the expanding mixture, it was verified that the adducts had the same stoichiometry. Since the overall appearance of the spectrum did not change appreciably as anisole pressure was varied between 0.3 and 3 Torr, the most likely stoichiometry of the adducts is 1:1. We shall return to this point in more detail in the Discussion section.

The feature at −1040 cm^{-1} (375.44 nm) appears in the spectra of both anthracene–anisole and anthracene–diethyl ether mixtures at exactly the same shift and with the same fine structure. Once formed, this feature persists even after the ether is removed from the apparatus, and all other bands disappear. It is found that its intensity increases sharply as the temperature of the anthracene crystals is increased. In view of these properties, it is tentatively assigned to a product formed due to the thermal interaction of anthracene with the ethers; one possibility is the formation of a product of anthracene, catalyzed by the presence of an ether. Since this feature evidently does not concern the main theme of the present work, we defer further discussion of its nature to future work.

Anthracene–Aliphatic Ethers. Some representative excitation spectra obtained for these systems are shown in Figure 3. Adducts between anthracene and diethyl ether show qualitatively similar spectral features to those observed in the anthracene–anisole system. Both broad and sharp features are obtained, excitation into which lead respectively, to broad, unstructured emission spectra and to well-resolved ones. Figure 4 shows the appearance of the emission spectra obtained upon excitation into the broad bands for both systems (2-methylanthracene adducts, discussed below, are also shown for comparison).

The anthracene–diethyl ether adduct differs from the anthracene–anisole adduct, in that only one broad excitation band is found. Also, the intensity ratio of the sharp peaks to the broad ones is five times larger than in the anisole adduct. The decay times obtained for fluorescence observed upon excitation into the narrow and broad bands are similar, respectively, to those found for the anisole adducts.

In the case of tetrahydrofuran, only narrow bands are observed, in spite of a search for broad band features. Excitation into these bands leads to banded fluorescence spectra and to a decay time of 20–25 ns.

Perylene–Ethers. With perylene as the aromatic hydrocarbon, adducts with either anisole or diethyl ether yielded only banded spectra (Figure 5). Decay times are close to those of bare perylene (~10 ns). The results with anisole are very similar to those previously reported by Castella et al.[5]

Adducts of Methylanthracene Derivatives with Ethers. Adducts of dimethylaniline (or ammonia) with anthracene display very similar fluorescence spectra as adducts of these amines with perylene.[5,7] The dissimilarity revealed in the case of ether adducts prompted us to study the properties of substituted anthracenes with ethers. In this paper we discuss methyl substitution. In particular, we were interested in checking the possibility that the well-known activity of the 9,10-positions of anthracenes are related to exciplex formation. Figure 6 shows the excitation spectra of 9-(and of 9,10)methyl-substituted anthracenes with anisole and diethyl ether. The only features found in these spectra are highly structured bands, which are much more congested than the corresponding anthracene bands. The emission spectra are in all cases structured, again resembling the case of anthracene adducts (when excited in the narrow bands). The decay times were normal

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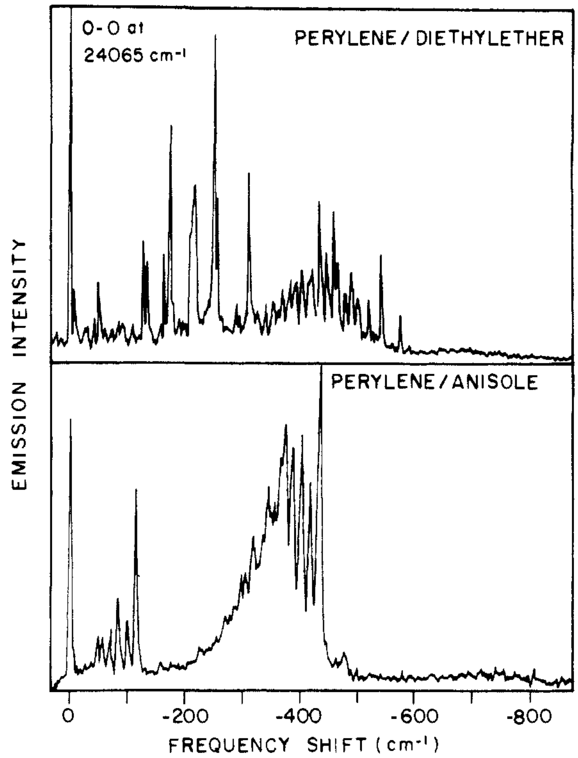

Figure 5. Excitation spectra of perylene–ether adducts. Observation is at 460 nm, time window 0–30 ns after excitation. Ether pressure was 1 Torr in both cases.

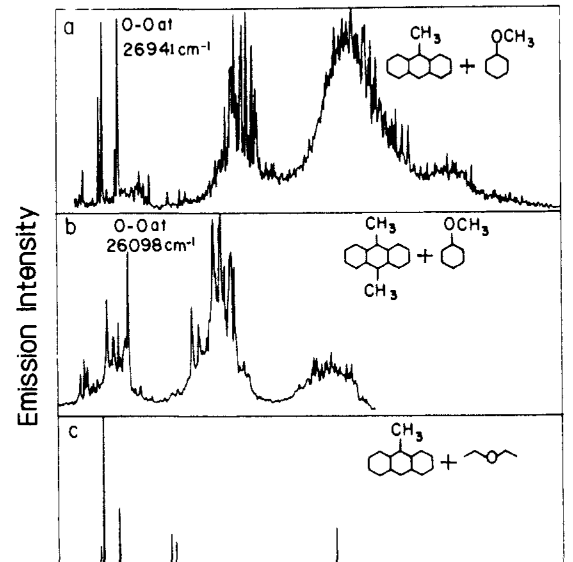

Figure 6. Excitation spectra of methyl-substituted anthracenes with anisole (top two panels) and with DEE (bottom panel). Observation wavelength 470 nm and time window 0–20 ns after excitation. (a) 9-Methylanthracene at 80 °C, anisole pressure 1 Torr. (b) 9,10-Dimethylanthracene at 100 °C, anisole pressure 1 Torr. (c) 9-Methylanthracene at 80 °C, DEE pressure 1 Torr.

(20–25 ns) for the diethyl ether adducts but significantly longer for anisole adducts. In fact, in this respect they resembled the broad bands of anthracene: decay times in some of the bands decreased from 40 ns near the red edge of the excitation spectrum to 20 ns near the blue edge.

With use of 2-methyl-substituted anthracene, fluorescence excitation (Figure 7) and emission (Figure 4, bottom 2 panels) spectra resembled those of unsubstituted anthracene. The bottom panel of Figure 7 shows essentially pure banded spectra, which are seen to be very congested. They may be distinguished from the broad bands (top panels of Figure 6) by two variables: shorter decay times (13–15 ns, compared to 35–45 ns) and different emission spectra. The band centered at a -600-cm^{-1} shift from the 0–0 band of the parent hydrocarbon is a representative of the broad bands. Its asymmetric shape resembles the case of anthracene–anisole adducts (cf. Figure 2)—at least two transitions are involved, but their splitting is smaller than their widths.

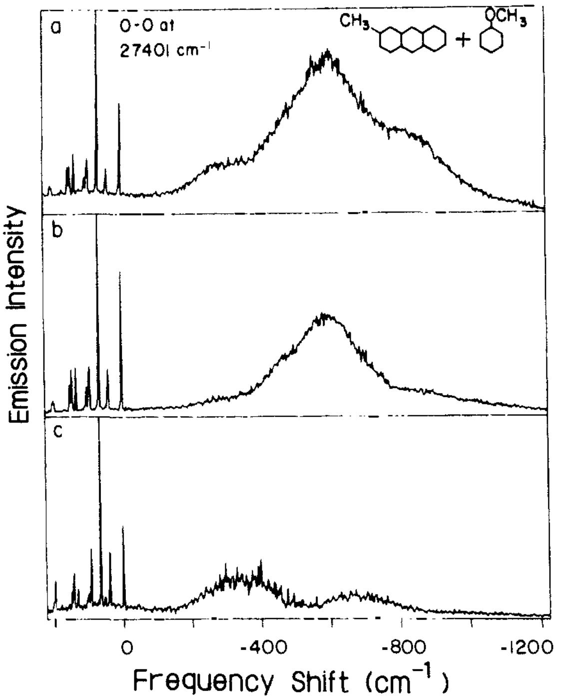

Figure 7. Excitation spectra of 2-methylanthracene–anisole adducts. 2-Methylanthracene held at 120 °C. Time window 20–40 ns after excitation. (a) Anisole pressure 2 Torr, observation at 470 nm. (b) Anisole pressure 1 Torr, observation at 470 nm. (c) Anisole pressure 2 Torr, observation at 405 nm.

Excitation spectra of 2-methylanthracene with diethyl ether are shown in Figure 8. The general appearance in this case again resembles anthracene adducts more than the 9-methylanthracene ones. This statement refers also to emission spectra and decay times (cf. Table I). However, two novel features should be mentioned. Comparison of panels a and b in Figure 8 shows that the intensity of the broad features to the red and blue of the strongest broad band centered around -700 decreases strongly upon reducing the ether pressure. This behavior is indicative of 1:2 (or higher) adducts. Furthermore, the excitation of the broad bands centered at -70 and -510 cm^{-1}, results in an emission that is very long-lived (~470 ns).

Discussion

Exciplexes and Locally Excited States. The identification of exciplex emission from jet-cooled adducts is based primarily on the fact that the emission spectrum of such species is very broad and strongly red shifted and lacks vibrational structure[4,8,18] (cf. Figure 1). In the present work, all of the pairs studied displayed well-structured absorption and emission spectra, characteristic of van der Waals bound locally excited species. In some cases, broad bands also appeared, always in addition to the narrow features. The presence of two separate band systems has been observed previously[5,7] and assigned to the co-existence of several structural isomers in the jet. In this work it is noted that broad emission bands appear only for anthracene and 2-methylanthracene adducts with anisole and diethyl ether. No such emission is found when perylene is used with these compounds,

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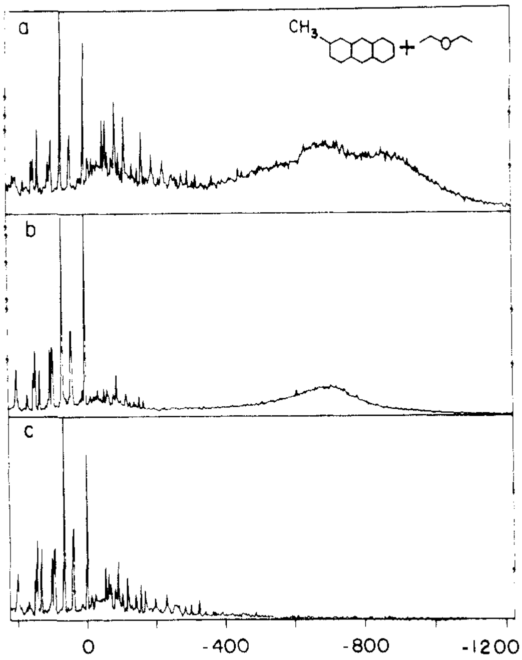

Figure 8. Excitation spectra of 2-methylanthracene–diethyl ether adducts. 2-Methylanthracene held at 120 °C. Time window 0–20 ns after excitation. (a) Ether pressure 2 Torr, observation at 470 nm. (b) Ether pressure 1 Torr, observation at 470 nm. (c) Ether pressure 2 Torr, observation at 405 nm.

while even with anthracene, tetrahydrofuran adducts show only LE-type spectra.

It has been noted that with amine donors[5-7] (dimethylaniline, aniline, and ammonia), exciplex-type emission displays a much longer decay time (100–500 ns) than the LE-type fluorescence. A similar trend is found in this work with ethers, but the difference is much less pronounced. The broad band emission has a decay time of up to 40 ns, while for the narrow bands, the lifetime does not exceed 25 ns. Notable exceptions are the 9-methylanthracene–anisole and 9,10-dimethylanthracene–anisole systems, in which only structural emission was found, but the decay times were about 35–40 ns.

We propose that exciplex formation takes place in some of these systems, and that it is determined largely by energetic and geometric considerations. In particular, the special reactivity of the 9,10-positions of anthracene helps in promoting the required electron transfer.

Curve Crossing Model and Geometric Considerations. The energy level diagram of Figure 1 is used to interpret the data. In principle, direct excitation of the CT state is possible; however, since the excitation spectra of the systems discussed in this paper are all relatively narrow and structured, it appears that such direct excitation is improbable. The curve crossing model, proposed for the amine systems,[5-7] can be extended so as to be suitable also for the ether systems. A prerequisite for exciplex formation by this mechanism is that the CT energy curve must cross the LE curve. The former may be calculated for any given separation R between the donor and the acceptor by

$$V_{CT} = C/R^{12} + I_D - EA_A - e^2/R - e^2(\alpha^+ + \alpha^-)/2R^4 + \ldots \quad (3)$$

where the first term represents a repulsive interaction, dominant at short intermolecular separations. The constant C is obtained from the well depth calculated by the pairwise potential method, assuming that the repulsive part of the potential is similar for the van der Waals and the CT states. I_D is the ionization potential of the donor, EA_A is the electron affinity of the acceptor, and α^+ and α^- are the polarizabilities of the cation D^+ and the anion A^-, respectively. Other terms may usually be neglected. The energy of the locally excited state may be calculated by assuming van der Waals stabilization of the first excited state of the bare molecule. Since van der Waals adducts of anthracene[19] and of perylene[20] normally display a red shift of only a few hundred wavenumbers, this stabilization is much smaller than that of the CT state.

Table I. Broad Excitation and Emission Bands Observed in Jet-Cooled Adducts between Aromatic Hydrocarbons and Ethers

system	0–0 transition[a] (cm^{-1})	excitation bands ν_{max}[b,c] (cm^{-1})	excitation bands fwhm (cm^{-1})	emission bands λ_{max}[c] (nm)	emission bands fwhm (cm^{-1})
anthracene–anisole	27 695	−1160	~250	440	4500
		−920	~250	440	4500
		−135	~250		
		+195			
anthracene–diethyl ether	27 695	−1032	~350	416 (s)	
				445	4600
				480 (s)	
		~0[d]			
2-methylanthracene–anisole	27 401	−860[e]	~300	445	3200
		−610			
		−590 (s)			
		−470[d]			
2-methylanthracene–diethyl ether	27 401	−700[f]	260	448	2500
		−510[g]	250		
		−70[g]			
anthracene–tetrahydrofuran	27 695	narrow bands only			
9-methylanthracene–anisole	26 939	narrow bands only[h]			
9-methylanthracene–diethyl ether	26 939	narrow bands only[h]			
9,10-dimethyl-anthracene–anisole	26 098	narrow bands only			
9,10-dimethyl-anthracene–diethyl ether	26 098	narrow bands only			
perylene–anisole	24 065	narrow bands only			
perylene–diethyl ether	24 065	narrow bands only			

[a] Of the bare hydrocarbon. [b] Expressed as the shift with respect to the 0–0 transition of the bare hydrocarbon. [c] s denotes shoulder. [d] This region is congested by narrow bands; a broad one may be present. [e] From anisole pressure dependence, this peak is probably due to a 1:2 adduct. [f] The fluorescence decay time upon excitation at this frequency was 46 ns. [g] These peaks are due to 1:2 adducts. The decay time measured upon excitation of these peaks was 470 ns. [h] Decay times vary across the excitation spectrum. They are about 40 ns near the red edge.

By using the appropriate parameters to calculate the potential curves according to eq 3, it is found that *all* of the systems studied in this work are energetically capable of forming exciplexes by the curve crossing mechanism. The fact that only few of them do, must be related to other factors.

Spectroscopic properties of jet-cooled adducts are known to be strongly dependent on their geometry.[21] The conformation of the ground-state adducts may be calculated by using pairwise atom–atom potentials.[22,23] In these calculations it is assumed that the geometry of the constituents does not change upon adduct formation, and only the relative positions of the two are varied

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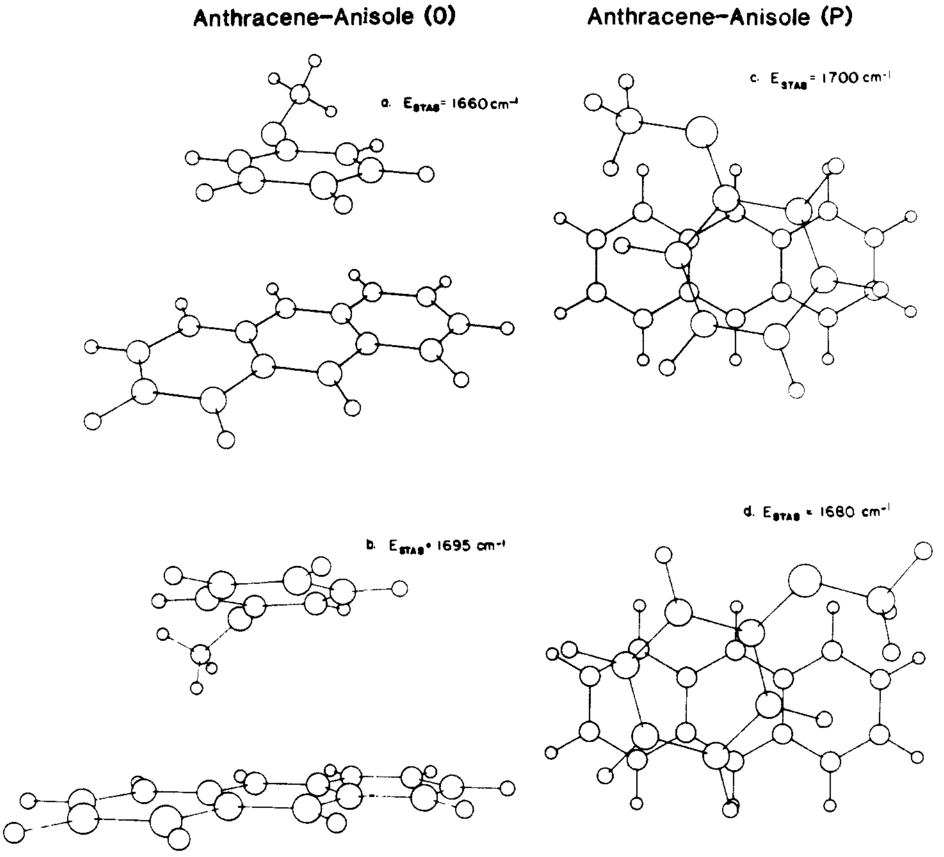

Figure 9. A graphic representation of the atom–atom pair potential calculations for anthracene–anisole adducts (O and P denote the orthogonal and planar forms of anisole; E_{stab} denotes the stabilization of the complex compared to the separated molecules). In all cases the interplanar distance is close to 4 Å. The aromatic planes are nearly parallel. (a, b) Two stable conformations of the anthracene–anisole (O) adduct. (c, d) Two stable conformations of the anthracene–anisole (P) adduct. In contrast to a, b these adducts are shown from "above" the anisole molecule in order to clearly show the differences in structure.

until energy minima are obtained. Lennard-Jones 6–12 potentials were used,[23b] with an added Coulombic electrostatic term in which the charge distribution within each constituent was explicitly considered.[23c] Such calculations, when applied to adducts of anthracene with ammonia,[7] revealed the presence of two types of species, one of which was much better oriented for electron transfer than the other.

Anisole has two conformational structures,[24] both of which may coexist in the jet, since they differ only slightly in their stabilization energies. The geometries of anisole-anthracene adducts as obtained from such additive pairwise atom–atom potential calculations is shown in cartoon form in Figure 9.

Each of the two anisole conformers is seen to lead to two distinct structures, differing only slightly in energy. Thus all of them may coexist in the jet, accounting for the four sets of bands (two structured and two broad, Figure 2) observed experimentally. It is noted that according to these calculations, the aromatic ring of anisole overlaps the anthracene skeleton, and the oxygen atom projects outside. This geometry is quite different from that calculated for amine adducts,[7,13] in which the nitrogen atom was found to be situated next to the center of the aromatic structure.

It is noted also that in some cases (Figure 9 (parts a and c)) the location of the oxygen atom is such that its lone pair orbitals can overlap reasonably well with the hydrogen atom attached to C9 of anthracene. Consequently, in this configuration the hydrogen atom may serve as a bridge since this helps to promote electron transfer. A similar interaction is believed to be involved in hydrogen bonding.[25]

In other structures (Figure 9 (parts b and d)) the interaction with the 9-position hydrogen is hindered, either by the anisole methyl group or by the fact that the lone pair faces away. If that interaction is important for exciplex formation, such structures lead to van der Waals, LE type fluorescence spectra. It should be noted that in all the calculations, minima in the potential surfaces were rather broad. This holds particularly for rotational motion of anisole with respect to anthracene around an axis perpendicular to the aromatic rings. Rotations by 10–20° raised the energy by only a few tens of cm^{-1}. This trend was found for the diethyl ether adducts discussed in the next paragraph.

The known structure of diethyl ether[26] leads, in a similar calculation, to the structure shown in Figure 10. Only one stable structure is obtained. The shape of diethyl ether assumed in these calculations is shown in the figure. Since rotations around single C–C bonds of diethyl ether in rather facile, nonplanar conformations of diethyl ether may also exist in the jet. The planar form may lead to electron transfer, since it allows close contact between the ether and anthracene. In the other forms the separation between the two is larger, and only van der Waals interaction can take place. It should be noted that in the calculations, most of the attraction between the hydrocarbon and the ether is due to carbon–carbon interaction, while the oxygen–carbon interaction is more repulsive in nature. Notice that the oxygen lone pair is found in this case, as in that of anisole, to be in close proximity to the 9-position hydrogen.

In the case of 9-methylanthracene–diethyl ether, the most stable calculated conformation is such that the oxygen atom is facing the methyl group. Notably, this system does not show exciplex-type emission. In the case of 9-methylanthracene–anisole, no such preference is found. In fact, eight different conformers, having rather similar energies, are obtained.

Tetrahydrofuran has essentially the same ionization potential (9.42 eV) as that of diethyl ether (9.50 eV). Its geometry is quite

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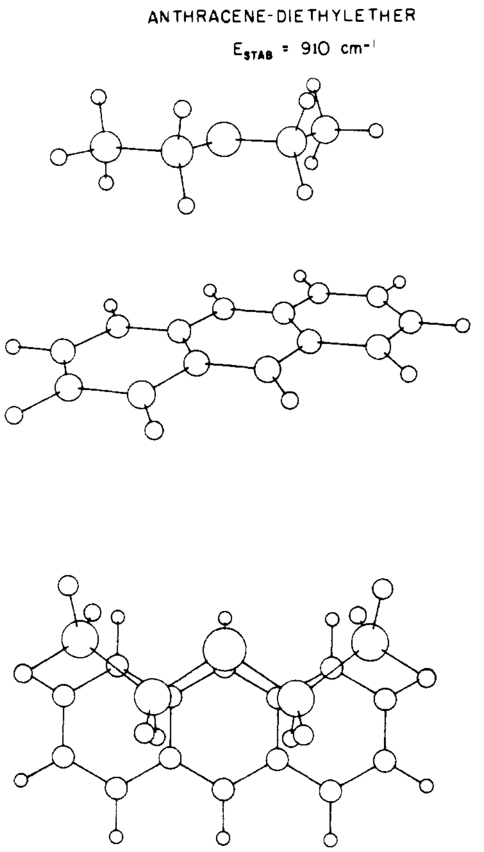

Figure 10. Two views of the anthracene–DEE adduct. The distance between the oxygen atom and the aromatic plane is 4.1 Å. (Note that the intermolecular distances obtained via the Lennard–Jones potential are usually larger than those obtained by the Buckingham potential; by using the latter, the distance is about 3.5 Å.)

different, and the calculation shows[27] that the most stable conformation of the anthracene–tetrahydrofuran adduct is such that the oxygen atom is situated next to the center of the aromatic skeleton. This configuration is not expected to result in strong interaction with the 9-position (assuming lone pair electrons are involved) unless a major conformational change takes place. Experimentally, only LE-type emission is observed for this system.

The Role of Anthracene 9,10-Positions. Comparison of the ether systems with amine[5-7] ones shows that the tendency for exciplex formation is stronger in the latter. This is reflected by the fact that in the bulk many amines, both aliphatic and aromatic, are known to form fluorescent exciplexes with aromatic hydrocarbons, while only a few cases of ether exciplexes are known.

As the discussion in the previous section suggests, the formation of ether exciplexes may be related to an interaction between the oxygen lone pair electrons and the active 9,10-positions of anthracene. Moreover, the symptoms characterizing exciplex emission are most prominent in cases where a hydrogen atom is attached to these positions and, in which, according to the orbital geometry calculations the oxygen lone pair is near enough to interact. Thus, we propose a working hypothesis emphasizing the role of 9-(or 10)substituted hydrogen in promoting exciplex formation with ethers. This hypothesis is based primarily on the following observations: (1) Anthracene and 2-methylanthracene show well-characterized exciplex emission with anisole and diethyl ether, while perylene and 9-methylanthracene do not. By comparison, adducts of the latter two with amines do show exciplex emission. (2) The anthracene–tetrahydrofuran adduct shows only van der Waals type emission. (3) The emission spectrum of 9-methylanthracene and 9,10-dimethylanthracene with anisole is structured, as for a van der Waals bound locally excited state, but the decay time is longer than measured for most van der Waals adducts. (4) The red shift of the ether systems leading to exciplex emission is systematically larger than that of the amine systems ($\sim$1000 cm^{-1} compared to $\sim$400 cm^{-1}), and the bands are broader ($\sim$300 cm^{-1} compared to $\sim$100 cm^{-1}).

These results can be qualitatively accounted for by considering the calculated structures of the ground-state adducts and the assumption that after light absorption near the origin of the electronic transition structural changes are slow. Thus, if electron transfer requires a major structural change, it will not take place. These considerations were discussed and demonstrated in the case of ammonia adducts.[7] The added assumption, namely that a hydrogen atom at an anthracenic 9-(or 10)position promotes electron transfer, is sufficient to account for the results presented in this work.

Consider, for example, the anisole–anthracene system. The two ground-state conformers arising from the ortho form are almost equally stable. In one of them, a lone pair orbital is seen to be pointing in the direction of the 9-hydrogen (Figure 9a) and in the other away from it (Figure 9b). A related situation holds for the planar form of anisole (Figure 9 (parts c and d); here the angular displacement is such that in one conformer the lone pair is close to the 9-hydrogen, and in the other it is further removed.

The case of tetrahydrofuran–anthracene adduct is also consistent with the model. The most stable calculated form is such that the oxygen atom is located in a plane that is perpendicular to the aromatic rings and contains the long axis of the anthracene molecule. The lone pair is facing away from the plane of the molecule and thus away from the 9,10-positions. Similarly, the fact that both anisole and ether are found to form exciplexes with 2-methylanthracene and less readily with 9-methylanthracene (see below) is consistent with the model.

Substitution of the 9-hydrogen with a methyl group (as well as with a chlorine atom[28]) leads to very congested but structured spectra with both anisole and diethyl ether. Thus, charge transfer and exciplex formation appear to be impeded. However, the fact that the decay times are anomalously long indicates that some interaction with the CT state may take place. One may possibly account for these findings by assuming that the excited state involved has a partial CT character, namely that its wave function may be represented as a superposition of the LE and CT states, eq 4, with $C_1 > C_2$. The contribution of the CT states is reflected in the longer than usual decay times and in strong congestion of the excitation bands. It should be noted that even in systems exhibiting broad emission and thus considered as basically due to a CT state, the decay times are much shorter than in the case of amine complexes. Furthermore, the decay time was found to depend not only on the excitation frequency but also on the emission wavelength, being longer toward the red edge (see, for instance, anthracene with anisole). If we assume in this case the mixed state (eq 4) with $C_2 > C_1$, the emission spectrum represents both components, with the LE contribution becoming more and more prominent at higher frequencies, presumably representing more favorable Franck–Condon factors.

$$\psi^* = C_1\psi_{LE} + C_2\psi_{CT} \qquad (4)$$

2-Methylanthracene–Diethyl Ether. This system shows a special feature, namely very long decay times (470 ns) observed upon excitation of some broad bands assignable to 1:2 adducts. The long decay times resemble the anthracene–ammonia system and may be construed as due to a state with a predominantly charge-transfer character. It is noted that a more red-shifted 1:2 adduct does lead to a "normal" short decay time (cf. Table I).

In terms of the energy level diagram of Figure 1, this behavior may be indicative of emission from states belonging only to the CT state, for instance, lying below the LE surface. The second ether molecule may serve as a bath for the excess energy, needing to be disposed of from the complex in order to reach such states. This could be obtained by a geometric rearrangement or even by

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[27] The structure of anthracene–tetrahydrofuran (THF) was calculated by assuming a puckered ring structure for THF, bond lengths, bond angles, and the pucker angle were taken from the following: Dieter, C. *Isr. J. Chem.* **1983**, *23*, 78. Hydrogen atoms were not included in the calculations.

[28] Anner, O.; Zaroura, E.; Haas, Y., to be published.

actual dissociation ($AD_2 \rightarrow AD + D$) in which the leaving molecule carries away the excess energy.

Summary

The emission properties of jet-cooled adducts between ethers and some aromatic hydrocarbons may be accounted for by assuming an excited state that is a superposition of a van der Waals locally excited (LE) state and a charge-transfer (CT) state. The direct optical transition from the ground state to the CT state is forbidden by either symmetry or Franck–Condon considerations. Thus, the excitation spectrum is dominated by the LE state, and emission from the CT state has a longer decay time. The CT character of the excited state is more prominent in anthracene and its derivatives than in perylene. This is particularly so when a hydrogen atom is bound to a C-9 or C-10 carbon. It is therefore proposed that this atom may serve as a bridge in transmitting the charge from the oxygen lone pair orbital of the ether. Geometric factors appear to be decisive in determining the interaction as shown by the fact that tetrahydrofuran, in which the oxygen atom is constrained to be away from the 9- or 10-position, does not show exciplex-type emission with anthracene.

Registry No. $(Et)_2O$, 60-29-7; PhOMe, 100-66-3; anthracene, 120-12-7; 2-methylanthracene, 613-12-7; 9-methylanthracene, 779-02-2; 9,10-dimethylanthracene, 781-43-1; perylene, 198-55-0; tetrahydrofuran, 109-99-9.

Preparation and Reactivity of Several Alkylidene Complexes of the Type W(CHR′)(N-2,6-C_6H_3-*i*-Pr_2)$(OR)_2$ and Related Tungstacyclobutane Complexes. Controlling Metathesis Activity through the Choice of Alkoxide Ligand

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Abstract: The reaction between W(C-*t*-Bu)(dme)Cl_3 and ArNH(TMS) (Ar = 2,6-C_6H_3-*i*-Pr_2) yields W(C-*t*-Bu)(NHAr)(dme)Cl_2. In the presence of a catalytic amount of triethylamine, W(C-*t*-Bu)(NHAr)(dme)Cl_2 is transformed into W(CH-*t*-Bu)(NAr)(dme)Cl_2 quantitatively. Derivatives of the type W(CH-*t*-Bu)(NAr)$(OR)_2$ [OR = O-*t*-Bu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, and $OC(CF_3)_2(CF_2CF_2CF_3)$] have been prepared. The X-ray structure of W(CHPh)(NAr)$[OCMe(CF_3)_2]_2$ (prepared by treating W(CHEt)(NAr)$[OCMe(CF_3)_2]_2$ with *cis*-β-methylstyrene) showed it to be pseudotetrahedral with a W=C bond of 1.859 (22) Å and an alkylidene ligand turned so H_α and the phenyl ring lie in the C_α–W–N plane with the phenyl ring pointing toward the imido nitrogen atom. (Structure parameters: a = 11.57 (3) Å, b = 12.719 (2) Å, c = 21.192 (9) Å, V = 3118.9 Å^3, space group = $P2_12_12_1$, Z = 4, with R_1 = 0.089, and R_2 = 0.096.) Addition of $Me_3SiCH{=}CH_2$ to W(CH-*t*-Bu)(NAr)$[OCMe(CF_3)_2]_2$ yielded the tungstacyclobutane complex W$[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ whose crystal structure showed it to be a pseudo trigonal bipyramid with an axial imido ligand and an equatorial, bent (29.9°), tungstacyclobutane ring with W–C bond lengths of 2.099 (11) and 2.066 (11) Å. (Structure parameters: a = 18.049 (4) Å, b = 12.224 (4) Å, c = 18.877 (5) Å, β = 114.86 (2)°, V = 3778.9 Å^3, space group $P2_1/n$, Z = 4, with R_1 = 0.054, and R_2 = 0.058.) Vinyltrimethylsilane is not metathesized; W$[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ loses only vinyltrimethylsilane in solution to give W$(CHSiMe_3)$(NAr)$[OCMe(CF_3)_2]_2$. W(CH-*t*-Bu)[(NAr)$[OCMe(CF_3)_2]_2$ reacts rapidly with *cis*-3-hexene to give a mixture of W(CHEt)(NAr)$[OCMe(CF_3)_2]_2$ and W[CHEtCHEtCHEt](NAr)$[OCMe(CF_3)_2]_2$; the latter loses 3-hexene completely in solution at 25 °C to give the former. W(CH-*t*-Bu)(NAr)$[OCMe_2(CF_3)]_2$ reacts much more slowly with an equilibrium mixture of *trans*- and *cis*-3-hexene to give W(CHEt)(NAr)$[OCMe_2(CF_3)]_2$ in a reaction that is first order in tungsten and first order in 3-hexene. W(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$ reacts very slowly with vinyltrimethylsilane and virtually not at all with *cis*-3-hexene, while W(CH-*t*-Bu)(NAr)$[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ reacts slowly with each to give unstable products. W(CH-*t*-Bu)(NAr)$[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ will react rapidly with ethylene, however, to give an unsubstituted tungstacyclobutane complex whose structure is analogous to that of W$[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$, except that the WC_3 ring is absolutely planar. (Structure parameters: a = 18.355 (10) Å, b = 9.513 (11) Å, c = 19.976 (26) Å, β = 96.75 (8)°, V = 3463.9 Å^3, space group $P2_1/n$, Z = 4, with R_1 = 0.076, and R_2 = 0.092.) An analogous W$(CH_2CH_2CH_2)$(NAr)$[OCMe(CF_3)_2]_2$ complex can be prepared. W(CH-*t*-Bu)(NAr)$(OR)_2$ complexes (where OR = O-*t*-Bu or $OCMe_2(CF_3)$) react with ethylene, but the ultimate products could not be characterized readily. Reactions involving 1-pentene in all cases are relatively complex. *cis*-2-Pentene is metathesized rapidly by $OCMe(CF_3)_2$ and $OCMe_2(CF_3)$ complexes. Unsubstituted tungstacycles react with PMe_3 to yield methylene complexes of the type W(CH_2)(NAr)$(OR)_2(PMe_3)$ [OR = $OCMe(CF_3)_2$ or $OC(CF_3)_2(CF_2CF_2CF_3)$].

For two decades the olefin metathesis reaction has elicited the sort of excitement that a totally new reaction deserves.[1] Since the classical catalyst systems based on Mo, W, or Re can be prepared easily, and in many cases exhibit extraordinarily high activity, classical catalysts found some applications relatively quickly, especially in the area of ring-opening metathesis polymerization of cyclic olefins. But olefin metathesis technology cannot be utilized fully until catalysts can be prepared systematically and their activity controlled by rational methods. Among the more frustrating of the problems is an incompatability of classical catalysts with a large number of functional groups.

The first evidence that the oxidation state of the metal in metathesis systems is probably the highest possible appeared in 1980; isolable complexes of the type W(CH-*t*-Bu)(O)L_2Cl_2 (L = a trialkylphosphine) were found to react with oridinary olefins in the presence of $AlCl_3$ to yield the expected new W(CHR′)-

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