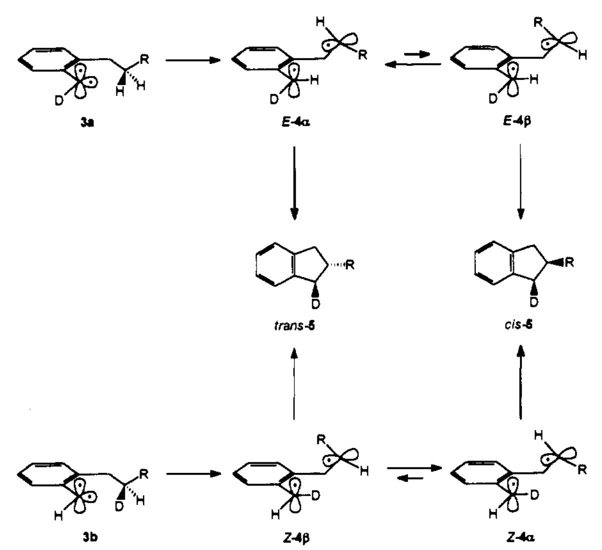
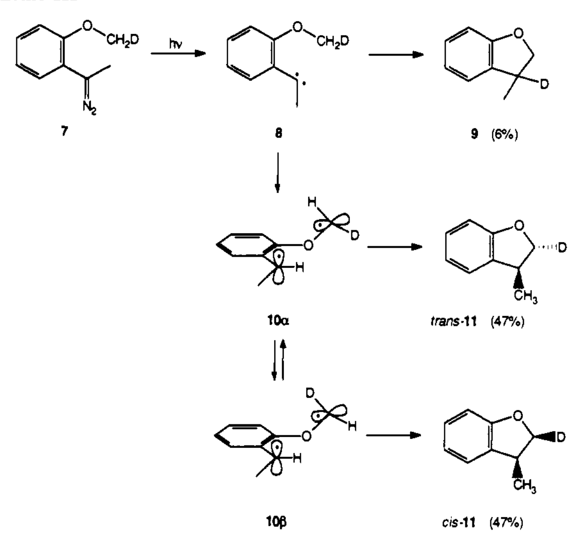
Scheme II



Scheme III



conformers, **4α** and **4β**, must then be considered for product formation. We suggest that the sterically less congested anti conformer **4α**, leading to pseudoequatorial orientation of R in the incipient indan, will be favored over the more congested syn (axial) conformer **4β** (Scheme II).

If these views are correct, the stereoselection should disappear in the case of R = D. The experiment was not practical with **4** (R = D) due to problems with product analysis. Therefore, we resorted to the deuterated (2-methoxyphenyl)methylcarbene **8** (Scheme III). The large isotope effect (k_H/k_D = 7.8) supports the abstraction–recombination mechanism for **8**. In contrast to **4**, the negligible energy difference between the biradical conformers **10α** and **10β** leads to a stereorandom distribution of deuterium in **11**.

In summary, an unprecedented steric discrimination between hydrogen and deuterium has been observed in the cyclization of carbene-derived 1,5-biradicals. In view of their magnitude and direction, the stereoselectivities cannot be correlated with the "effective size" of the hydrogen isotopes.[9] Our data demonstrate that pre-existing energy differences between conformers of the biradicals control the preferred mode of cyclization.[3a–c]

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(8) ESR detection and ab initio computation of the rotational barriers in (aryloxy)methyl radicals support this notion: Casarini, D.; Lunazzi, L.; Placucci, G.; Venturini, A. *J. Org. Chem.* **1991**, *56*, 414.

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Novel Structure of Langmuir–Blodgett Films of Chloroplatinic Acid Using *n*-Octadecylamine: Evidence for Interdigitation of Hydrocarbon Chains[†]

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Received August 25, 1992

We report for the first time the deposition of crystalline Langmuir–Blodgett (LB) films[1] with a novel X-ray diffraction pattern using *n*-octadecylamine monolayers at the air–water interface and chloroplatinic acid in the aqueous subphase. Evidence is given for an interdigitation of hydrocarbon chains in the new structure.

The π–A isotherms of *n*-octadecylamine spread at the air–water interface at pH = 4.0 and 9.0 in the presence and absence of H_2PtCl_6 (10^{-4} M solution) in the aqueous subphase are shown in Figure 1. It is well-known[2,3] that in acidic medium the π–A isotherms of *n*-octadecylamine are governed by the nature of the complex formed with the acid. In the presence of H_2PtCl_6 at pH = 4.0, the π–A isotherms show a large liquid expanded phase extending up to an area of ~34 Å^2/molecule compared to that at pH = 9.0 (~30 Å^2/molecule). The extrapolated area of ~34 Å^2/molecule in Figure 1a in the presence of H_2PtCl_6 is close to the basal plane area per Cl_6 octahedral unit reported for the layered perovskite structure of $(R-NH_3)_2MCl_4$ compounds.[4] It is likely that at low pressures the $(R-NH_3)Pt_{0.5}Cl_3$ monolayer is derived from the $(R-NH_3)_2MCl_4$ monolayer with vacancies at $R-NH_3$, M, and axial Cl sites. In the initial stages of compression the close-packed chloride ions of the layered perovskite imparts rigidity to a single monolayer. The area per mole of amine in the solid condensed phase at pH = 4.0 (~15–17 Å^2/molecule) is nearly half that at pH = 9.0 (~28 Å^2/molecule). The formation of a bilayer of the amine at the air–water interface is indicated at high pressures.

The octadecylamine–H_2PtCl_6 surface layers are easily deposited at pH = 4.0 onto a substrate (HF-treated Si(111) in this study; chromic acid treated quartz or glass plates gave the same results) at 30 dyn/cm using an oleic acid piston and a homemade apparatus.[5] The unusual feature is that *the oleic acid piston is displaced by an area equal to the area of the substrate only during the upward movement and not during the downward movement* (see insert of Figure 1a). This fact and the low area per mole at the deposition pressure shows clearly that a *bilayer* is deposited during the upward movement. Interferometric studies as well as ellipsometric studies (assuming a refractive index of 1.5) of the deposited (31 dips, 1 dip = upward + downward movement) multilayers gave a thickness of 28 ± 3 Å/dip. The infrared spectrum shows prominent CH_2 bands at ~2919 and 2850 cm^{-1}. The frequencies and relative intensities of these bands correspond well with those reported for crystalline LB films.[2]

The X-ray diffraction pattern (Figure 2) is novel for an LB film. It may be indexed on the basis of a repeat unit along the *c* axis with a separation of 27.05 ± 0.02 Å. We propose the body-centered unit cell (*c* parameter = 54.02 Å) of Figure 1b for the $(R-NH_3)_2MCl_6$ formula unit. The calculated intensities of

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[†] Communication No. 5430 from National Chemical Laboratory, Pune, India.

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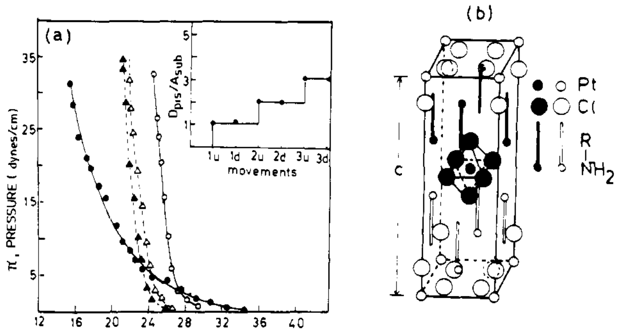

Figure 1. (a) π–A isotherms of *n*-octadecylamine monolayers at the air–water interface (solid line, pH = 4.0; dashed line, pH = 9.0) in the presence (filled points) or absence (open points) of H_2PtCl_6 in the aqueous subphase. Inset shows the displacement of oleic acid piston (D_{pis}) per unit area of substrate (A_{sub}) during the *n*th upward (*n*u) and downward (*n*d) movements. (b) Proposed unit cell structure of the Langmuir–Blodgett film deposited on the substrate (filled circles correspond to one deposition during an upward dip).

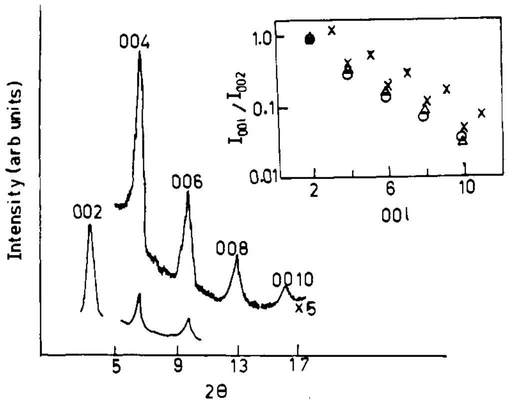

Figure 2. X-ray diffraction pattern of the LB film after 31 dips. Inset: The ratio of the X-ray diffraction intensities, I_{00l}/I_{002}, as measured (triangles) is compared with that calculated (circles) for the cell proposed in Figure 1b. The characteristic "odd–even" intensity oscillation of the 00*l* reflections of a typical Langmuir–Blodgett film of lead arachidate is also shown (crosses) for comparison.

the 00*l* reflections match well with those experimentally observed (shown in the inset of Figure 2) for the *z* coordinates given below:

$$Pt_{0.5}Cl_2\text{–}Cl\text{–}NH_3\text{–}(CH_2)_n$$

$$z = 0,\ 0.096,\ 0.098,\ 0.098\ +\ n(0.046)\ (n = 1\text{–}18)$$

$$(CH_2)_n \qquad\qquad -NH_3\text{–}Cl\text{–}Pt_{0.5}Cl_2$$

$$z = 0.098\ +\ n(0.046)\ (n = 0\text{–}17),\ 0.926,\ 0.904,\ 1.00$$

Any model involving a disordered arrangement of bilayers with the hydrocarbon chains resting on top of another would necessarily give rise to a ~54-Å separation between the planes in which the 00*l* reflections with *l* = odd would be present. We propose that in the upward movement the $(R\text{-}NH_3)_2PtCl_6$ bilayer is incorporated with the $PtCl_6$ unit attached to the substrate. There is very little net deposition in the downward movement.

The multilayer films are not patchy as they do not show any Si from the substrate in X-ray photoelectron spectra (VG ESCA-3 spectrometer, unmonochromatized Al Kα radiation). Of interest to us is the location of the $[PtCl_6]^{2-}$ unit. The ratio I_{30}/I_{70} of the Pt 4f as well as Cl 2p intensities at the two tilt angles of 30° (I_{30}) and 70° (I_{70}) (with respect to the plane of the surface) from such multilayer films is nearly 0.30 in both cases. In terms of the discrete layer model developed by us,[5] a value of I_{30}/I_{70} = 0.30–0.40 signals the location of the species at a depth equivalent to the length of one hydrocarbon chain from the surface. The N 1s spectrum[6] shows two features. One of these is a shoulder at a binding energy of 400 eV characteristic of NH_2 groups, and there is a prominent peak at ~403 eV characteristic of NH_3^+ groups. The NH_3^+ component of the N 1s spectrum also behaves in the same manner. The Pt, Cl, and N at this level are in the ratio of nearly 1:6:2 (after normalizing for the scattering cross sections). The intensities of two prominent C 1s lines and the N 1s line at ~400 eV relative to platinum increase at low takeoff angles (I_{30}/I_{70} = 1.0–1.3), showing that they are on top of the platinum layer. A prominent signal from the O 1s region typical of bound water is only at the surface since it is not seen in the infrared spectrum. Results of detailed studies on the C 1s and N 1s XPS spectra as well as infrared spectroscopic studies are to be presented in another communication.

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C–F Bond Cleavage in C_6F_5X Arenes by Carbonyl-Stabilized Phosphorus Ylides. Synthesis of $Ph_3P{=}C(C_6F_4X\text{-}4)R$ (X = CN or NO_2). Crystal and Molecular Structure of $Ph_3P{=}C(C_6F_4CN\text{-}4)CO_2Et$

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Received June 8, 1992

Some examples of C–F bond cleavage in fluoroarenes C_6F_5X, especially those containing electron-withdrawing substituents X such as CN or NO_2, have been reported in the literature.[1-8] This cleavage always occurs following the attack on the arene by a strong nucleophile [amines,[1] X^- (X = Cl, Br, I),[2] CN^-, MeO^-,[3] OH^-,[4] $CF_3CH_2O^-$,[5] C_6H_5NNH,[6] $Ph_2PCH_2P({=}NSiMe_3)Ph_2$,[7] or N_3^-[8]]. Most of these reactions require energetic conditions and give the para-substituted products. A para F–C bond cleavage has been suggested to account for the polymerization of $(C_6F_5)Me_2P{=}CH_2$.[9a] Here we report the first unambiguous examples of C–F bond cleavage in fluoroarenes by phosphorus ylides. An additional noteworthy feature of these reactions is that they occur at room temperature in spite of the weak nucleophilic character of the ylides studied. Some ortho-F-substitution reactions have been described as the result of intramolecular heteroatom (such as Pt[10] or N[11]) assisted processes.

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