The structure of **1** has been determined by X-ray crystallography.[9] **1** crystallizes in the orthorhombic space group $Pna2_1$ with four molecules per unit cell. An ORTEP view of the molecule is shown in Figure 1. There are several interesting features. The molecular structure consists of a Cr_3 triangle capped on each face by a μ_3-S atom with three edge bridging μ_2-S atoms. The Cr-$(\mu_2$-S$)_3$ core is virtually planar[10] while the two μ_3-S atoms are almost equally positioned above and below this plane (1.774 Å, av).[10] Each Cr atom bears a bidentate chelating dmpe ligand resulting in an overall distorted octahedral coordination geometry. There is a distinct deviation from an idealized D_{3h} symmetry which can be attributed to a Jahn–Teller distortion (see below). The distortion is reflected in the Cr-Cr and Cr-S distances. Thus Cr(1)-Cr(2) is notably longer than either Cr(1)-Cr(3) or Cr-(2)-Cr(3) (2.647 (7) vs. 2.552 (6) and 2.565 (8) Å, respectively). The Cr-S(μ_3) distances also reflect this distortion with Cr(1)-S(1) and Cr(2)-S(1) longer than Cr(3)-S(1) (2.323 (8) and 2.421 (11) vs. 2.208 (9) Å, respectively). The S(2) atom is more symmetrically displaced and in this case the distortion brings it closer to Cr(1) and Cr(2) and away from Cr(3) (Cr(1)-S(2) = 2.309 (9), Cr(2)-S(2) = 2.325 (13), Cr(3)-S(2) = 2.340 (13) Å). The Cr-S(μ_2) distances also fall into two distinct regions Cr(1)-S(3) and Cr(2)-S(3) (2.429 Å, av) and are both notably longer than the other Cr-μ_2-S bond lengths (2.340 Å, av). All of these distances are in the normally observed ranges for Cr-S bonds (ca. 2.2–2.4 Å).[4]

The Cr-P distances also fall within two distinct ranges. Those to Cr(1) and Cr(2) are noticably shorter (2.292 (12)–2.393 (9) Å) than those to Cr(3) (2.435 (14) and 2.454 (10) Å).

The coordination geometry about each Cr atom is roughly octahedral. Thus typical trans angles subtended at Cr(1) S-(3)-Cr(1)-S(5), S(1)-Cr(1)-P(1), and S(2)-Cr(1)-P(2) are 173.3 (4)°, 170.0 (4)°, and 171.4 (4)°, respectively. The cis angles P(1)-Cr(1)-P(2), S(1)-Cr(1)-P(2), and S(2)-Cr(1)-S(1) are 82.1 (3)°, 88.3 (3)°, and 100.1 (3)°, respectively.

Regarding each S atom as a dianion gives eight d electrons for **1**. Extended Hückel calculations[11] were carried out on a model compound, $Cr_3S_5(PH_3)_6$, at D_{3h} symmetry where all bond lengths and angles have been averaged from the experimental structure for **1**. The valence, metal-centered orbitals are shown from a top view in Figure 2. The lowest three orbitals, a_1' and e', are σ-bonding. At higher energy the a_1'' is π antibonding and e'' is π bonding. The a_1'' level lies at a lower energy than e'' because one combination of lone pairs on the μ_2-S atoms has a large overlap

with e'' and destabilizes it. There is no S combination that matches the symmetry of a_1''. Calculations[12] on $Mo_3S_2Cl_9{}^{3-}$, an isoelectronic molecule, give the same level pattern and relative energies except that e'' lies slightly lower in energy than a_1''. The μ_2-Cl lone pairs are much weaker π donors than S. A first-order Jahn–Teller distortion occurs in this complex giving two long and one short Mo–Mo bond lengths.[13] In our system the 0.62-eV energy gap between the HOMO and LUMO is relatively small and signals a possible second-order Jahn–Teller distortion. Allowing the Cr(1)-Cr(2) distance to increase while the Cr(1)-Cr(3) and Cr(2)-Cr(3) bonds contract reduces the molecular symmetry to C_{2v}. The A component of e'' mixes into a_1'' with the phases shown in Figure 2 to increase the π bonding between Cr(1) and Cr(3) along with Cr(2) and Cr(3). This stabilizes a_1'' and provides an electronic rationale for the distortion observed in **1**.

Further studies on phosphine-stabilized sulfido clusters of the transition metals are in progress.

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Metal–Metal Double-Bond Formation and Control of Cluster Geometry via Steric Design: Syntheses and Structures of the First Ir4 Arsenido and Phosphido Complexes: Planar Unsaturated [Ir(μ-*t*-Bu2As)]4(μ-CO)2(CO)2(Ir≡Ir) and Tetrahedral Saturated [Ir(μ-Cy2P)CO]4(μ-CO)2 (Cy = Cyclohexyl)

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We have previously shown that the use of bulky bridging phosphido (R_2P^-) or arsenido (R_2As^-) ligands can dramatically alter the stoichiometries, structures, and reactivites of their d-block transition-metal complexes.[2] We describe here the synthesis, structures, and characterization of [Ir(μ-*t*-Bu2As)]4(CO)2(μ-CO)2 (**1**) and [Ir(μ-Cy2P)(CO)]4(μ-CO)2 (**3**), which, to our knowledge are the first tetranuclear Ir arsenido and phosphido stabilized clusters to be reported (Scheme I).[3,4]

(1) Alfred P. Sloan Foundation Fellow, 1985–1987.

(2) See, for example: Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard A. J. *J. Am. Chem. Soc.* **1985**, *107*, 888. Kang, S.-K.; Albright, T. A.; Jones, R. A.; Wright, T. C. *Organometallics* **1985**, *4*, 666. Jones, R. A.; Wright, T. C. *Organometallics* **1983** *2*, 1842. Jones, R. A.; Lasch, J. G.;Norman N. C.; Whittlesey, B. R.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6184.

(3) Few other Ir phosphido species are known. Ir(COD)(μ-pz)(μ-Ph2P)2Ir(C8H13) (pzH = pyrazole; COD = 1,5-cyclooctadiene): Bushnell, G. W.; Stobart, S. R.; Vefghi, R.; Zaworotko, M. J. *J. Chem., Soc. Chem. Commun.* **1984**, 282. See also, for Ir3(μ-PPh)(CO)6(Ph)(dppm): Harding, M. M.; Nicholls, B. S.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1983**, 1479. For the phosphinidene complex Ir4(μ3-PhP)(μ2-CO)3(PPh3)4: Demartin, F.; Manassero, M.; Sansoni, M.; Giarlaschelli, L.; Sartorelli, U. *J. Organomet. Chem.* **1981**, *204*, C10.

(8) Full experimental details will be published separately. Yield 20%, **1** crystallizes from toluene (–20 °C) as black prisms; mp >360 °C, IR (KBr disk) 2934 (m), 2897 (s), 1410 (s), 1290 (m), 1271 (s), 1262 (s), 1095 (br, m), 1022 (br, m), 984 (w), 943 (s), 927 (s), 891 (m), 801 (m), 739 (w), 707 (m), 670 (w), 645 (m), 411 (m), 400 (m), 307 (w), 250 (m), 226 (s) cm^{-1}. ^{1}H NMR (90 MHz in Me2SO-d_6) δ 1.40 m, 36 H, CH3; δ 1.69 m, 12 H, CH2. ^{31}P{^{1}H} (In Me2SO-d_6 at 32.34 MHz), δ 48.83 (relative 85% H3PO4 (aq), δ 0.0). Microanal. Calcd C, 28.20%; H, 6.31%; P, 24.24%. Found: C, 28.12%; H, 6.40%; P, 23.56%. There is no IR spectroscopic evidence for the presence of S-H and the complex is EPR silent at room temperature and at –196 °C in toluene. The effective magnetic moment at room temperature μ_{eff} = 0.0 μ_B. (Evans method, toluene). These data and the sharpness of the ^{31}P NMR signal rule out the possibility of a paramagnetic Cr(III)(III)(III) formulation for **1**.

(9) CAD-4, the crystal data: $C_{18}H_{48}Cr_3P_6S_5$; M_r = 766.74, orthorhombic, $Pna2_1$ (No. 33), a = 20.754 (3) Å, b = 9.103 (7) Å, c = 18.443 (4) Å, U = 3484.3 (5) Å^3, D_c = 1.462 g cm^{-3}, Z = 4, (Mo Kα) = 0.71073 Å (graphite monochromator), μ = 14.68 cm^{-1}. Methods: MULTAN, difference Fourier, full-matrix least squares. Refinement of 1483 unique observed reflections ($I > 3\sigma I$) out of 1584 measured (2° < 2θ < 50°), gives current R and R_w values of 0.072 and 0.080, respectively. All non-hydrogen atoms were refined anisotropically, H atoms were not located. The largest peak in the final difference Fourier was 0.8 e Å^{-3}.

(10) Deviations (Å) from the least-squares plane through Cr(1), Cr(2), Cr(3), S(3), S(4), and S(5) are Cr(1) –0.003 (4), Cr(2) 0.025 (6), Cr(3) –0.011 (4), S(3) –0.010 (11), S(4) –0.008 (8), and S(1) –1.764 (7), S(2) 1.784 (7). A complete listing of all bond lengths and angles is available. See paragraph at end of paper regarding supplementary material.

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Scheme I. Synthesis of Ir_4 Arsenido and Phosphido Clusters
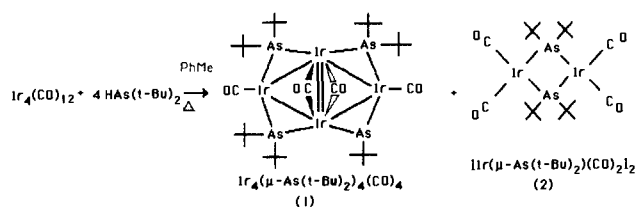
These complexes are parrticularly noteworthy for several reasons. Their isolation and characterization demonstrate that it should be generally possible to control the geometry of the metal atom frameworks of larger clusters ($M > 3$) by the judicious use of sterically demanding ligands. The fact that (1) has a planar Ir_4 core and (3) a tetrahedral, closed core reflects the relative streric demands of the μ-t-Bu_2As^- and μ-Cy_2P^- units. The former is much more sterically demanding and so forces the four Ir atoms into an open, planar array also reducing the number of CO ligands bound to the cluster (4 vs. 6). In 3 the Cy_2P^- groups cause less steric hindrance and the metals adopt a closed tetrahedral geometry and achieve a formal 18-electron count. The interaction of $Ir_4(CO)_{12}$ with t-Bu_2PH under similar conditions produces two complexes of lower nuclearity: $Ir_3(\mu$-$Bu_2P)_3(CO)_5$ (4) and [Ir-$(CO)(t$-$Bu_2PH)]_2(\mu$-$H)(\mu$-t-$Bu_2P)$ (5). This is consistent with
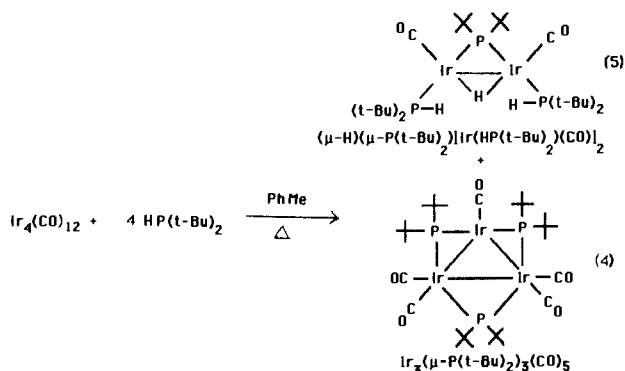
our proposal since t-Bu_2P^- is even more sterically demanding than t-Bu_2As^- or Cy_2P^-. (4) and (5) will be described elsewhere.[5] Of key interest in 1 is the presence of an isolated Ir=Ir double bond in a planar Ir_4 arrangement. There are few transition-metal clusters with three or more metals which contain multiple bonds.[6] Examples include derivatives of the Re_3^{9+} core such as $Cs_3Re_3Cl_{12}^{6,7}$ while for carbonyl clusters there are a mere handful including $Os_3(CO)_{10}(\mu$-$H)_2$,[8] $Re_4(CO)_{12}(\mu$-$H)_4$,[9] [Re$_3$-$(CO)_{10}H_3]^{2-}$,[10] and $[Re_3(CO)_{10}H_4]^-$.[11] To our knowledge, 1 is the first Ir cluster containing a localized Ir=Ir double bond and only the second planar Ir_4 cluster so far discovered.[12]

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(11) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1977**, *136*, C49. (Re=Re = 2.821 (7) Å.)
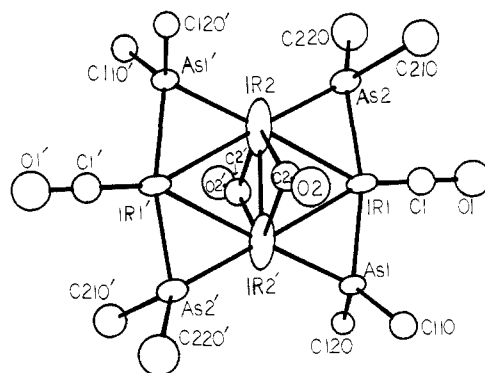
Figure 1. ORTEP view of 1. Methyl groups have been omitted for clarity. Key bond lengths (Å) and angles (deg) for 1: Ir(1)–Ir(2) 2.807 (3), Ir(1)–Ir(2)' 2.866 (3), Ir(1)–As(1) 2.361 (4), Ir(1)–As(2) 2.384 (4), Ir(1)–C(1) 1.66 (5), Ir(2)'–As(1) 2.411 (4), Ir(2)–As(2) 2.406 (5); Ir(2) –Ir(1)–Ir(2)' 54.4 (1), Ir(1)–Ir(2)–Ir(2)' 64.0 (1), Ir(1)–As(1)–Ir(2)' 72.0 (1), Ir(1)–As(2)–Ir(2) 73.5 (1). Ir(2)–C(2)–Ir(2)' 71 (1). Complete listings are provided as supplementary material.[19]
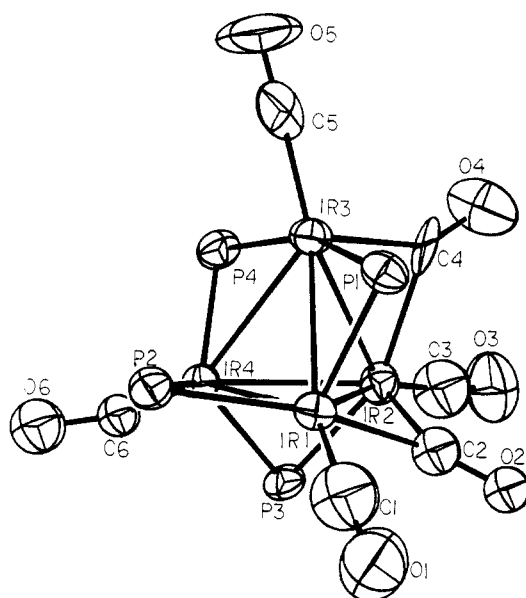
Figure 2. ORTEP view of the central core of 3. Cyclohexyl groups have been omitted for clarity. Key bond lengths (Å) and angles (deg) for 3: Ir(1)–Ir(2) 2.811 (2), Ir(1)–Ir(3) 2.855 (2), Ir(1)–Ir(4) 2.769 (2), Ir-(2)–Ir(3) 2.784 (3), Ir(2)–Ir(4) 2.807 (3), Ir(3)–Ir(4) 2.882 (2); Ir-(1)–P(2)–Ir(4) 73.9 (4), Ir(1)–P(1)–Ir(3) 76.7 (4), Ir(2)–P(3)–Ir(4) 74.8 (4), Ir(3)–P(4)–Ir(4) 76.8 (4). Complete listings are provided as supplementary material.[19]

The reaction of $Ir_4(CO)_{12}$ with 4 equiv of t-Bu_2AsH in refluxing toluene (12 h) results in a very dark red, almost black solution from which $[Ir(\mu$-t-$Bu_2As)]_4(\mu$-$CO)_2(CO)_2$ (1) may be isolated (43% yield)[13] (see Scheme I). Also formed in this reaction is the yellow dimer $[Ir(\mu$-t-$Bu_2As)(CO)_2]_2$ (2) (12%). The reaction of

(12) To our knowledge, the only other planar Ir_4 cluster structurally characterized is [Ir$_4$(CO)$_8${(MeCO$_2$)$_2$C$_2$}$_4$]: Heveldt, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 340. Of related interest is the planar Rh_4 phosphinidene complex [Rh(COD)]$_4$(μ_4-PPh)$_2$: Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1251. See also, for [Rh$_4$(CO)$_5$(μ-PPh$_2$)$_5$]$^-$ which contains a Rh$_4$ tetrahedron: Kreter P. E., Jr.; Meek, D. W.; Christoph, G. G. *J. Organomet. Chem.* **1980**, *188*, C27. See also, for planar Os$_4$(CO)$_{14}$(PMe$_3$): Martin, L. R.; Einstien, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1986**, *108*, 338. For planar Os$_4$-(CO)$_{13}$(μ_3-S): Adams, R. D.; Horvath, I. T.; Segmüller, B. E.; Young, L. W. *Organometallics* **1983**, *2*, 1301.

(13) Evaporation to dryness, extraction of the residue into hexane, and cooling (−20 °C) produced 1 and 2. They may be separated by fractional crystallization since 1 is considerably less soluble than 2. Similar workup and recrystallization was used for 3. Details of characterization are provided in the supplementary material.[19] Full details of 2 will be published elsewhere.[15]

$Ir_4(CO)_{12}$ with Cy_2PH under similar conditions gives deep red $[Ir(\mu\text{-}Cy_2P)(CO)]_4(CO)_2$ (3) in 65% yield.[13] The structures of

$$Ir_4(CO)_{12} + 4\,Cy_2PH \xrightarrow[\Delta]{PhMe} Ir_4(\mu\text{-}Cy_2P)_4(CO)_6 \quad (3)$$
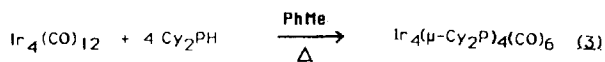
these complexes have been determined by X-ray crystallography.[14] The dimer $[Ir(\mu\text{-}t\text{-}Bu_2As)(CO)_2]_2$ (2) has two planar 16-electron Ir atoms, each bearing two CO ligands and bridged by two *t*-Bu$_2$As units. It will be described fully in another paper.[15] 1 is a black crystalline material which is air stable for short periods in the solid state but decomposes in solution when exposed to the air.

There are several unique features of the molecular structure of 1 (Figure 1). The central Ir_4 core is planar due to a crystallographically imposed center of inversion at the midpoint of $Ir(2)\text{-}Ir(2)'$. The two central Ir atoms $Ir(2)$ and $Ir(2)'$ are separated by a relatively short distance (2.592 (6) Å) which is consistent with an Ir=Ir double bond. The distance is similar to those observed in $[Ir(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (2.545 (1) Å)[5] and $[Ir(\mu\text{-}Ph_2P)(CO)(PPh_3)]_2$[4] (2.551 (1) Å) which both have Ir=Ir double bonds. The Ir=Ir double bond is bridged by two notably asymmetric CO ligands ($Ir(2)\text{-}C(2) = 2.08$ (4) Å, $Ir(2)'\text{-}C(2) = 2.36$ (4) Å).

The Ir–Ir distances around the outer edges of the Ir_4 parallelogram are typical of single bonds ($Ir(1)\text{-}Ir(2) = 2.807$ (3) Å, $Ir(1)\text{-}Ir(2)' = 2.866$ (3) Å). The *t*-Bu$_2$As$^-$ groups are virtually coplanar with the Ir_4 core and occupy slightly asymmetric bridging positions ($Ir(1)\text{-}As(av) = 2.373$ Å, $Ir(2)\text{-}As(av) = 2.409$ Å). The two Ir atoms at the far corners of the parallelogram ($Ir(1)$ and $Ir(1)'$) each bear a terminal CO ligand and have formal electron counts of 16. Of related interest to 1 is $Rh_6(CO)_{11}(\mu\text{-}t\text{-}Bu_2As)_2(\mu_4\text{-}t\text{-}BuAs)$ in which the use of the bulky *t*-Bu$_2$As$^-$ ligand results in a planar array of five rhodium atoms.[17]

The structure of the Cy_2P^- complex $[Ir(\mu\text{-}Cy_2P)(CO]_4(\mu\text{-}CO)_2$ (3) is quite different from that of 1 (Figure 2). The central Ir_4 core consists of a fairly regular closed tetrahedron. Four Cy_2P^- units bridge four edges of the tetrahedron and each Ir atom bears a terminal CO ligand. The two remaining edges of the Ir_4 tetrahedron are bridged by CO groups. Ir–Ir distances range from 2.769 (2) to 2.882 (2) Å and are typical of Ir–Ir single bonds. The Cy_2P^- units occupy fairly symmetrical bridging positions with the Ir–P distances ranging from 2.259 (11) to 2.341 (11) Å. These values may be compared to similar ones found in $[Ir(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$[5] [2.324 (2) Å] and $[Ir(\mu\text{-}Ph_2P)(CO)(PPh_3)]_2$ [2.288 Å (av)]. The $^{31}P\{^1H\}$ NMR of 3 shows four second-order multiplets with downfield shifts relative to 85% H_3PO_4 (aq).[13] This is consistent with the phosphido groups bridging metal–metal bonding distances.[18] The spectrum is consistent with the X-ray structure since all four P atoms are magnetically inequivalent and it has been successfully simulated.[19]

These results indicate that it should be possible to rationally synthesize unsaturated transition-metal clusters with a variety of open or planar central cores by using suitably bulky ligands. Further studies are in progress.

(14) Details of the X-ray structures of 1 and 3 are provided as supplementary material.[19]

(15) Jones, R. A.; Whittlesey, B. R., manuscript in preparation.

(16) For 1, deviations (Å) from the least-squares plane containing Ir(1), Ir(2), Ir(1)', Ir(2)', As(1), As(2), and C(1) are As(1) 0.179 (10), As(2) 0.028 (11), C(1) 0.234 (98). Deviation (Å) from the Ir(2)–Ir(2)'–C(2) plane for O(2) is 0.110 (76).

(17) Jones, R. A.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1985,** *107,* 1078.

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(19) See paragraph at end of paper regarding supplementary material.

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Kinetic Evidence for a Critical Hydrophobic Interaction Concentration

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Isobaric and isothermal activation parameters of organic reactions in water-rich mixtures of water with a relatively hydrophobic cosolvent have often shown complex, if not capricious, behavior upon variation of the solvent composition.[1,2] These intriguing effects have been attributed to the unique solvent structural properties of water.[3] In particular, the large and partially compensatory changes in enthalpies and entropies of activation are caused by initial state solvation effects and are believed to reflect hydrophobic interactions with the cosolvent.[1,2] Much emphasis has been placed on the *t*-BuOH–H$_2$O system. In a recent theoretical study, Grunwald[4] has analyzed the partial molar thermodynamic properties of this mixture in terms of two additive terms. The first "isodelphic", term refers to effects under conditions where the solvent network theoretically remains constant upon addition of *t*-BuOH; the second, "lyodelphic", term describes the effect of the change in the solvent network upon changing the molality of the cosolvent. In this paper we describe kinetic evidence in support of Grunwald's analysis and we introduce the concept of "critical hydrophobic interaction concentration" (chic).

Rate constants and isobaric activation parameters for the pH-independent hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole (1)
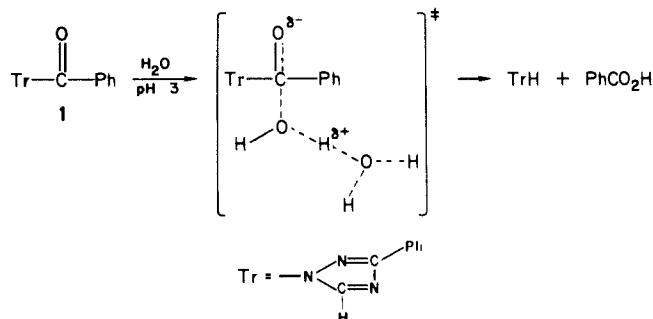
in highly aqueous *t*-BuOH–H$_2$O are summarized in Table I. The hydrolytic process, which occurs via rate-determining water-catalyzed nucleophilic attack of water on the carbonyl moiety,[5] is slowed down by the cosolvent. The plots of $\Delta^{\ddagger}H^{\ominus}$ and $\Delta^{\ddagger}S^{\ominus}$ vs. mole fraction of water (n_{H_2O}) exhibit the usual extrema at about 5 mol % of *t*-BuOH (Figure 1), attributable to lyodelphic solvent effects. The important observation is *that the large changes in* $\Delta^{\ddagger}H^{\ominus}$ *and* $\Delta^{\ddagger}S^{\ominus}$ *set in only below* $n_{H_2O} = 0.98$. It is only at $n_{H_2O} = 0.97$ that these changes are accompanied by a large heat capacity of activation[6] ($\Delta^{\ddagger}C_p^{\ominus} = -1200 \pm 200$ J mol^{-1} K^{-1}).

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