To determine if adducts might be formed in these systems via a route involving triplet energy transfer followed by addition of alkene triplets to ground-state enone, triplet AN was generated by BP sensitization in the presence of **2** (0.2 M) in neat AN under conditions where BP (1.0 M) absorbed >97% of the incident excitation. Only AN dimers were formed under these conditions; no adducts of AN to **2** could be detected. Thus, occurrence of triplet excitation transfer as the electron donor/acceptor properties of the alkene are varied cannot explain our data.

Spectroscopic analysis indicates that photoadducts of enones **2-5** with AN, FN, and CAN are annelation products and not oxetanes,[19] but their regio- and stereochemistry have yet to be established. Such adducts are also formed with cycloheptenone,[20] which does not form adducts with electron-rich alkenes.[1] We believe that widespread acceptance of the exciplex hypothesis[5] has inhibited exploration of the utility of photocycloadditions of enones to electron-poor alkenes in synthetic methodology.[21]

Thus, despite the undeniable heuristic value of the exciplex hypothesis,[5] the intermediacy in enone photoannelations of Corey's "oriented π-complex"[1] is not supported by our kinetic data. A distinction between direct formation of triplet biradicals and the involvement, at least in some cases, of a prior intermediate must await the results of further kinetic studies.

Acknowledgment. The National Science Foundation (CHE-8320154) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are thanked for grants in support of the research at NYU. N.J.T. thanks NSF and AFOSR for generous support of the research at Columbia.

(19) In particular, GC/MS, NMR, and FT-IR spectra of separated products as well as product mixtures show, respectively, the proper mass and molecular fragmentation patterns characteristic of [2 + 2] cycloadducts, the absence of vinyl hydrogens, and the presence of the carbonyl moiety. Full details will be given in the full paper to be published later.

(20) Stoute, V. A.; Shimonov, J.; Schuster, D. I. Unpublished results.

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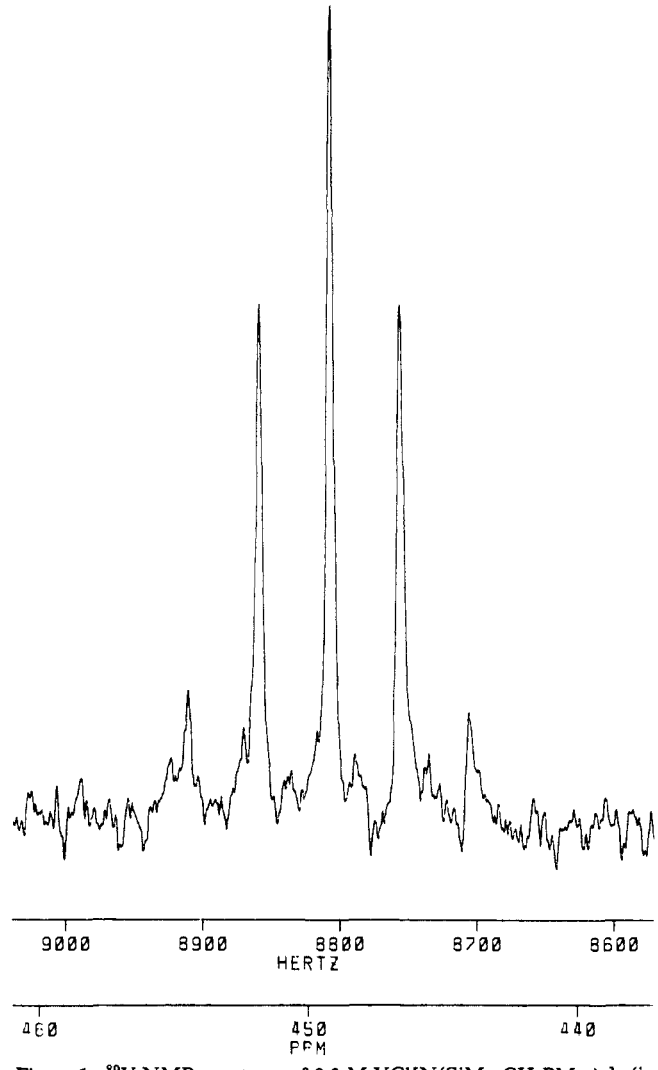

Figure 1. ^{89}Y NMR spectrum of 0.3 M $YCl[N(SiMe_2CH_2PMe_2)_2]_2$ (in C_7D_8-THF; (70:30) relative to aqueous YCl_3 at 0 ppm. The spectrum was obtained with a 20-ms pulse and a 2-s acquisition time over a total time of 10 h.

Phosphine Complexes of Yttrium(III). Synthesis, Reactivity, and Fluxional Behavior of $YCl[N(SiMe_2CH_2PMe_2)_2]_2$

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There are no phosphine coordination compounds of the group 3 element yttrium.[1] In fact, if one looks to the lanthanoid metals, to which yttrium is often compared because of its similar physiochemical properties,[2] a conclusion easily reached is that phosphine ligands are not well suited[3] for complexes of these elements. Arguments based on *hard* and *soft*, that is, mismatching of donors and acceptors, undoubtedly have some merit since the prototypical ligands for these hard metal centers are oxygen- and nitrogen-based.[1] Given the fact that the phosphine donor has played a pivotal role in the development of the coordination chemistry of the transition elements,[4] we set out to prepare phosphine complexes of the early transition elements and the lanthanoid metals. We were confident that new chemistry and reactivity patterns would emerge simply because the choice of ligands around a metal is one of the most important factors in tuning a metal's chemical behavior.

An already proven protocol for the introduction of phosphine ligands onto the group 4 metals, Zr(IV) and Hf(IV), is the use of a chelating array containing the disilylamido donor flanked by two phosphine ligands as shown in the bis(ligand) complexes[5] **1** and the monoligand derivatives[6] **2**. Our strategy for the design of this ligand type was to take advantage of the ability of the amide donor to anchor the chelate array on Zr(IV) and Hf(IV) and force

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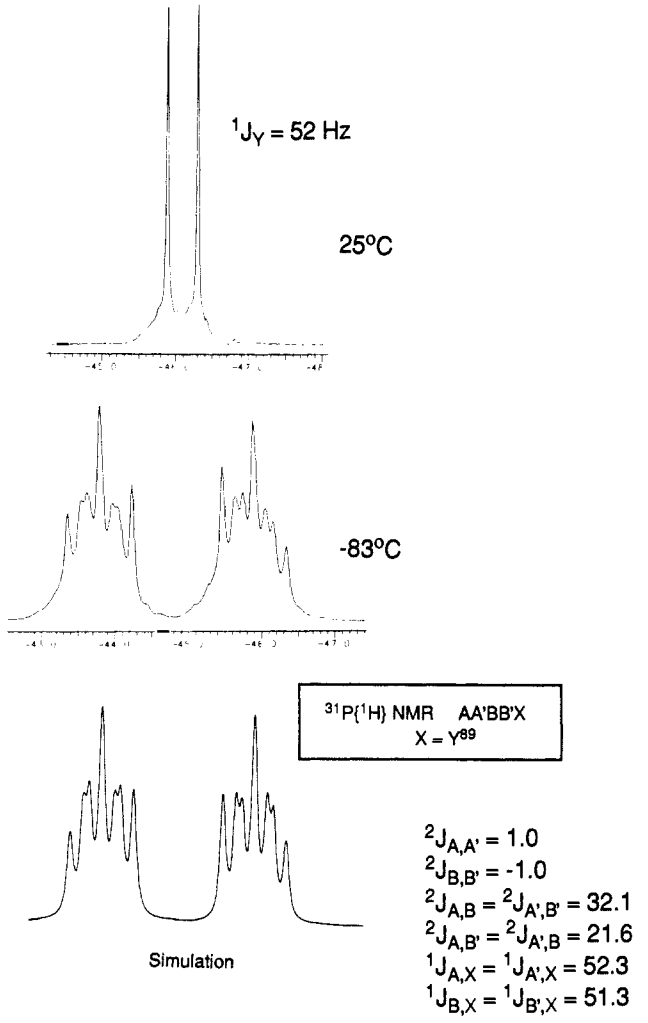
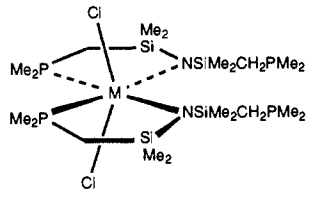
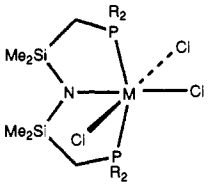


Figure 2. $^{31}P\{^1H\}$ NMR spectra of $YCl[N(SiMe_2CH_2PMe_2)_2]_2$ (in C_7D_8) as a function of temperature: (a) ambient temperature, (b) −83 °C, (c) simulation of limiting spectrum with the indicated parameters.

phosphine coordination by virtue of the chelate effect. This strategy also obtains for yttrium(III).



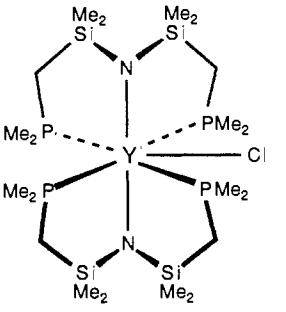
1 M = Zr, Hf



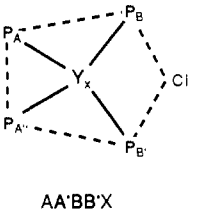
2 M = Zr, Hf; R = Me, Pr^i

Anhydrous YCl_3 reacts with 2 equiv of $LiN(SiMe_2CH_2PMe_2)_2$ in THF to generate a seven-coordinate hexanes-soluble, monomeric complex of the formula $YCl[N(SiMe_2CH_2PMe_2)_2]_2$, **3**. *This is the first reported yttrium phosphine complex.* A particularly attractive feature of yttrium is that ^{89}Y has a spin of 1/2 and is 100% naturally abundant.[7] Indeed, the $^{31}P\{^1H\}$ NMR spectrum at 25 °C shows a doublet with yttrium to phosphorus coupling ($^1J_{Y-P}$ = 52 Hz). Moreover, the ^{89}Y NMR spectrum of this complex shows the expected binomial quintet with the same coupling (Figure 1); it is interesting to note that the ^{89}Y chemical shift of +449 ppm relative to aqueous YCl_3 indicates a strong deshielding by this ligand system.[7]

Seven coordination usually implies fluxional behavior,[8] and this is true for this yttrium complex; cooling the sample and monitoring by $^{31}P\{^1H\}$ NMR spectroscopy shows that the doublet broadens and coalesces at −50 °C into a more complex pattern (Figure 2) which can be analyzed as a AA'BB'X spin system (A,A',B,B' = ^{31}P; X = ^{89}Y). The ^1H NMR and ^{13}C NMR spectra also show consistent temperature-dependent behavior (vide infra) but are not well resolved even at −100 °C. There are a number of possible shapes to use in discussing geometry for seven-coordinate molecules, for example, capped octahedral, pentagonal bipyramid, and capped trigonal prism.[9] With the information from the low-temperature $^{31}P\{^1H\}$ NMR spectrum, it is tempting to speculate on a possible solution structure in the slow-exchange limit. On the assumption that the smaller the ^{31}P–^{31}P couplings are the more cisoid the disposition of the phosphorus donors, and conversely, the larger the couplings the more transoid the disposition, we favor a geometry based on a distorted pentagonal bipyramid as shown below. As it turns out, the bulky disilylamido groups are trans in this assumed geometry. However, in the absence of crystallographic data to provide a basis for a static structure, this is still conjecture.[10] If we make the above assumption as to the geometry in the low-temperature limit, then we can infer that the nature of the fluxional behavior which exchanges the phosphorus environments probably involves phosphine dissociation. This is based on the following observations: (i) the ^1H NMR spectrum of **3**



3



in the fast-exchange limit consists of three singlets: the silylmethyl ($Si(CH_3)_2$), methylene (PCH_2Si), and phosphorus methyl ($P(CH_3)_2$) protons; thus, the fact that we observe no coupling to phosphorus-31, particularly for the phosphorus methyls and methylene protons, is indicative of extremely weakly bound phosphine donors; and (ii) the geometry assumed above for **3** is chiral, and at low temperature there is evidence for diastereotopic silylmethyls and phosphorus methyls, albeit the signals are quite broad. To racemize this assumed geometry given the constraints of the two tridentate ligands is best accomplished by a series of dissociative steps involving the phosphine arms of the tridentate ligand. Other pseudorotation type rearrangements without phosphine dissociation are of course possible but require a traverse through a convoluted manifold of geometries.[9]

The remaining chloride of this bis(ligand)yttrium(III) phosphine complex (**3**) is metathesizable by aryllithium and alkylpotassium reagents to generate a series of organoyttrium derivatives[11] as shown in the equation. This fact was somewhat surprising to us

$$YCl[N(SiMe_2CH_2PMe_2)_2]_2 + RM \rightarrow YR[N(SiMe_2CH_2PMe_2)_2]_2$$

RM = PhLi, RM = $PhCH_2K$

4, R = Ph
5, R = CH_2Ph

since we had been thwarted earlier in our efforts to metathesize the chlorides of the bis(ligand) complexes of Zr and Hf (i.e., **1**)

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(10) Another possibility is a capped trigonal prism with the Cl ligand as the cap and the tridentate ligands sitting on the triangular faces also giving a molecule with C_2 symmetry.
(11) For other examples of organoyttrium derivatives, see: (a) Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. J. *Organometallics* **1987**, *6*, 2279 and references therein. (b) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053.

although the monoligand complexes of the group 4 metals, **2**, are quite reactive in this regard. The phenyl complex **4** and the corresponding benzyl derivative **5** display analogous solution behavior as the starting chloride complex **3**, in that, at room temperature one observes a doublet in the $^{31}P\{^1H\}$ NMR spectrum which broadens at low temperature to an AA'BB'X spin system.

Now that the door to phosphine complexes of yttrium has been opened, we will endeavor to extend this methodology to the lanthanoid metals.[3] This is already in progress.[12]

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Supplementary Material Available: Experimental, microanalytical, and ^1H, ^{13}C, and ^{31}P NMR data for all new compounds (4 pages). Ordering information is given on any current masthead page.

(12) Fryzuk, M. D.; Haddad, T. S.; Berg, D. G., unpublished results.

Proton Transfer Is Not Rate-Limiting in Buffer-Induced Nonenzymic Glucation of Hemoglobin

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The reaction of glucose with amino groups in proteins occurs nonenzymically[1] in vivo. This intrinsically very slow process appears to be critical in the pathogenesis of various secondary complications associated with diabetes mellitis[1,2] and in the process of aging,[3] so that its mechanistic features are important to understand. The paradigmatic reaction of glucose with hemoglobin has been extensively studied and is known[4] to occur most rapidly at the N-terminal valine of the β-subunit. An initial, rapid imine formation is succeeded by slower Amadori rearrangement to the final aminoketone[5] (Figure 1).

The reaction is accelerated by several buffers,[6] including phosphate buffer (Figure 2). This catalysis, or similar effects by other species present in the biological environment, may lead to as much as a doubling of the rate of protein damage at the aggregate concentrations of several millimolar expected for such species. In fact, general acid–base catalysis by buffer is expected for the proton-abstraction and proton-donation steps at the Amadori rearrangement. However, we find that the phosphate-dependent reaction occurs with identical rate constants in protium oxide, deuterium oxide, and with either glucose-*2-h* or glucose-*2-d* as reactant (Figure 2). This absence of either solvent or substrate isotope effect *excludes as a rate-limiting step BOTH proton-transfer steps of the general acid–base-catalyzed Amadori rearrangement* (i.e., proton abstraction by buffer, which would show a substrate isotope effect, and proton donation by buffer, which would show a solvent isotope effect). Thus the buffer

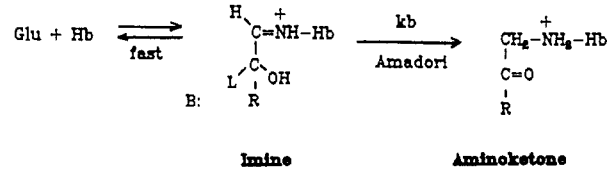

Figure 1. Mechanistic scheme for the nonenzymic glucation of proteins. L represents the substrate label (H or D) in D-glucose. When B abstracts H to form BH^+ in DOD as solvent, rapid exchange should produce BD^+. Thus the proton-donation step in HOH will involve BH^+; in DOD it will involve BD^+.

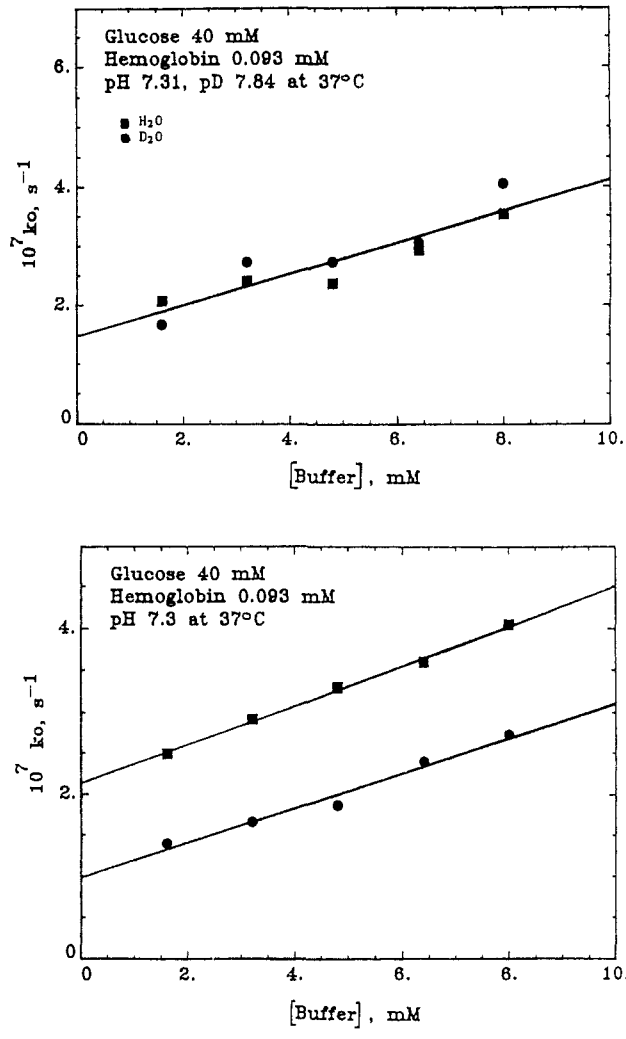

Figure 2. Top: First-order rate constants for the reaction of 40 mM D-glucose with hemoglobin in protium and deuterium oxides at pH 7.3, pD 7.8, 37°C, in sodium phosphate buffers at the indicated total buffer concentrations. The line shown fits the data for both HOH and DOD, corresponding to $k_{HOH}/k_{DOD} = 1.0$ for both buffer-independent and buffer-dependent rates. When the two data sets are fitted independently, 10^7k_{HOH}, s^{-1} = (1.63 ± 0.23) + (0.215 ± 0.034) [buffer, mM], and 10^7k_{DOD}, s^{-1} = (1.32 ± 0.34) + (0.317 ± 0.064) [buffer, mM]. Bottom: First-order rate constants for the reaction of 40 mM D-glucose-*2-h* (upper line, 10^7k_o, s^{-1} = (2.13 ± 0.04) + (0.238 ± 0.008) [buffer, mM]) and D-glucose-*2-d* (lower line, 10^7k_o, s^{-1} = (0.98 ± 0.10) + (0.214 ± 0.019) [buffer, mM]) with hemoglobin at pH 7.3, 37 °C. The rate constants in the bottom plot were determined from data over a substantial portion of the reaction and are thus of higher quality than those in the top plot, which were evaluated from only two time points; this probably accounts for the differences between the data for D-glucose-*2-h* in HOH in the top and bottom plots.

acceleration of the rate is not classical, protolytic general acid–base catalysis. Instead, some other process (conceivably a buffer-induced change in the conformation of the hemoglobin-glucose imine, although since it is not certain that this process would lack a solvent isotope effect, such a conclusion cannot be made with

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