excited-state interaction between the pyrene and the anilinium fraction. In addition, the exclusive CT fluorescence from 1 in the free-base form in polar media indicates rapid conversion of the pyrene localized π, π^* state to the CT state.¹¹ Finally, transient data (discussed below) indicate that deprotonation of the conjugate acid, in the pyrene localized π,π^* state, also leads to formation of the CT state. These observations are consistent with the photophysical scheme shown in Figure 1.

The fluorescence decay of the short-wavelength emission (conjugate acid form) is a simple exponential under all conditions in aqueous media. At sufficiently high pH to completely deprotonate the ground state, the long-wavelength fluorescence also shows exponential decay behavior. But, in the pH range where both conjugate acid and free base are present in the ground state, the long-wavelength fluorescence is a composite of a fast and slower decay. The fast component arises from direct excitation of molecules in the free-base form to the pyrene localized π,π^* state, which rapidly relaxes to the CT state. The slow component results from excitation of molecules in the conjugate acid form which undergo excited-state deprotonation to the locally excited pyrene free-base state with subsequent rapid relaxation to the CT state (see Figure 1). This latter fluorescence component displays the lifetime characteristics of the longer lived conjugate acid fluorescence. Consistent with this scheme is the observation that even at pH values sufficient to protonate all of 1 in the ground state, a long-wavelength (CT) fluorescence is still noted. This fluorescence can only arise by the deprotonation route. There is no evidence that the CT state directly returns to the locally excited π,π^* state (either free base or protonated). This irreversibility is understandable in terms of the extreme endothermicity of this process ($\geq 0.7 \text{ eV}$).

At sufficiently low pH values¹² that all of **1** is protonated, the efficiency of the CT state fluorescence shows a pH dependence indicating proton-transfer quenching. In alcohol-water over the pH range 1-2, a linear Stern-Volmer plot of the relative CT fluorescence yield vs. [HCl] $[\gamma_{\pm}^2]^{14,15}$ is observed with a slope indicating $k_Q = (4.9 \pm 0.8) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Proton-transfer quenching has also been observed with the aminonaphthalenes¹⁶ and 1-aminopyrene.¹⁷ In the methoxynaphthalenes,¹⁶ it has been shown via H/D isotope labeling experiments that the quenching occurs with protonation of the ring carbons of naphthalene as expected for the molecule in its CT state. We believe that our observations with 1 represent the first example of proton-transfer quenching of a twisted CT state which, although geometrically different from the arylamine CT states, would also be expected to react by way of protonation of the pyrene ring.

Under conditions where all of 1 in the ground state is in the protonated form, the composite quantum yield for the short

(11) The similarity of the UV-visible absorption spectra of 1 in nonpolar and polar media indicates that in all media excitation occurs to a pyrene (12) The "pH" values, obtained with a Markson S-585 semimicro com-

bination pH/reference glass electrode, provide a reliable measure of relative acidities of aqueous ethanol solutions.¹³ The measured pH is related to the hydrogen ion activity, referenced to the standard state in aqueous ethanol, by $pa_{H}^{*} = pH - \delta$ where δ is essentially constant for a particular solvent composition. In turn $\delta = (\bar{E}_j - \log_{m} \gamma_H)$ where \bar{E}_j is the residual liquid junction potential in pH units and $_{m} \gamma_H$ is the medium effect for hydrogen ion. For 50 wt% ethanol-water, δ has been variously reported as 0.17, 0.21, and 0.29,¹³ which indicates the range of discrepancy between pa_{H}^{*} and pH as well as the magnitude of correction that may be applied to the pK, values in Table I. (13) Bates, R. G. "Determination of pH. Theory and Practice", 2nd ed.;

Wiley: New York, 1973; pp 243-251 and references therein.

(14) In this quantity, γ_{\pm} is the mean activity coefficient for HCl in 50% (v/v) aqueous ethanol interpolated from the data of Ivanov, A. I.; Slovetskii, V. I.; Shevelev, A. A.; Fainzil'berg, A. A.; Novikov, S. S. Izv. Akad. Nauk SSSR, Ser. Khim. 1967, 61.

(15) Harris and Selinger (Harris, C. M.; Selinger, B. K. J. Phys. Chem. **1980**, 84, 891) recently pointed out that the rate of proton-transfer quenching shows a dependence on $[H^+](\gamma_{\pm})^{-2Z_1}$, where Z_1 is the charge on the species being quenched, because of the influence of the ionic environment. The dependence on γ_{\pm}^2 in our system may reflect an interaction between the proton quencher and the pyrene radical anion moiety of the CT state ($Z_1 = -1$). (16) Tobita, S.; Shizuka, H. Chem. Phys. Lett. **1980**, 75, 140.

(17) Shizuka, H.: Tsutsumi, K.; Takeuchi, H.; Tanaka, I. Chem. Phys. 1981, 59, 183.

Table I. Ground- and Excited-State Acidities

system	pK _a	pK _a *	
1-(p-aminophenyl)pyrene by Forster cycle by fluorescence titration aniline 1-aminopyrene 1-aminonaphthalene	4.05 4.58^{a} 2.8^{b} 3.9^{d} 4.1^{d}	3.3 3.6 -1.2^{c} -1.0^{d} 0.8^{d}	_
2-annionaphinatene	7 ,1	-0.0	

^a In methanol.⁵ ^b In water.⁶ ^c In acetonitrile-water, 50:50.⁷ ^d In acetonitrile-water, 5:95.⁸

(protonated) and long (CT) wavelength fluorescences (Φ_c) was measured (relative to quinine sulfate as a standard). The intrinsic quantum efficiency (Φ_{CT}°) of the long-wavelength fluorescence was determined under pH conditions where all of 1 is in the free-base form. The expected quantum yield for the long-wavelength fluorescence under the actual experimental conditions (Φ_{CT}) was determined by correcting Φ_{CT}° for the proton-transfer fluorescence quenching at the specific pH of the medium. The quantum efficiency for deprotonation of the excited conjugate acid (Φ_{-H^+}) can be shown to be given by

$$\Phi_{-H^{+}} = (\Phi_{c}/\Phi_{CT})(A_{CT})/A_{c}$$
(1)

where A_c and A_{CT} are the areas of the composite and longwavelength fluorescences, respectively. The rate constant for the deprotonation step is defined by

$$k_{-\rm H^+} = \Phi_{-\rm H^+} / \tau_{\rm sw}$$
 (2)

where τ_{sw} is the lifetime of the short-wavelength fluorescence. In alcohol-water, $k_{-H^+} = (1.9 \pm 0.4) \times 10^7 \text{ s}^{-1}$ (determined at pH 1.1).

In conclusion, we wish to emphasize the special electronic and geometric features in this system, as summarized in Figure 1, that allow the relatively simple measurement of proton-transfer rates. We are currently investigating the use of 1 as a probe of the influence of the microenvironment on absolute rates of proton transfer.

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Registry No. 1, 87393-65-5.

Novel Syntheses of α,β -Unsaturated Cyclopentenones via Allylzincation of Alkynes¹

Ei-ichi Negishi* and Joseph A. Miller

Department of Chemistry, Purdue University West Lafayette, Indiana 47907 Received June 27, 1983

Although virtually untested, cis carbometalation of alkynes with functionally substituted organometallic reagents can produce alkenylmetal derivatives (1) that may serve as intermediates for cycloalkenes (eq 1). In view of the significance of α,β -unsaturated



R, $R^1 = H$, C, or hetero atom group; $R^2 = C$ group X = functional group M = metal group

⁽¹⁰⁾ Eigen, M. Angew. Chem., Int. Ed. Engl. 1964, 3, 1.

⁽¹⁾ Selective Carbon-Carbon Bond Formation via Transition Metal Catalysis. 37. Controlled Carbometalation. 16. Part 15: Negishi, E.; Van Horn, D. E.; Yoshida, T.; Rand, C. L. Organometallics 1983, 2, 563.

cyclopentenes both as structural units in natural products and as intermediates for their synthesis, we were attracted by the following potential routes to two representative classes of α,β -unsaturated cyclopentenones 2 and 3 involving allylmetalation of alkynes (eq 2). Unfortunately, however, the scope of the al-



lylmetalation of alkynes in the literature was surprisingly limited.² Aluminum³ and copper,² two metals that have been most widely used for carbometalation of alkynes, do not readily undergo allylmetalation. In fact, all our attempts at observing their allylmetalation have failed.⁴ Although allylzincation of terminal alkynes is known,^{2,5} it is invariably accompanied by alkynyl hydrogen abstraction, and the corresponding reaction of internal alkynes is essentially unknown.⁶ Allylboration of alkynes⁷ appears to be the only allylmetalation in the literature that gives singlestage allylmetalation products uncomplicated by any side reactions. Here again, however, internal alkynes appear to be inert, unless strongly activated by electron-donating groups such as alkoxy.

We have found the reaction of allylzinc bromide, generated in situ from allyl bromide and zinc, with 1-trimethylsilyl-1-octyne in THF for 18-24 h at 60 °C produces, after treatment with iodine, an 83% yield of 1-iodo-1-(trimethylsilyl)-2-n-hexyl-1,4pentadiene⁸ (4a) as an 85:15 mixture of the Z and E isomers.⁹ The regioselectivity of the reaction is essentially 100% as judged by a combination of ¹H and ¹³C NMR and GLC. When 5-decyne was used in place of 1-(trimethylsilyl)-1-octyne, no carbometalation took place under comparable reaction conditions. Therefore, the Me₃Si group plays a critical role in inducing the observed carbometalation. Hydroboration of 4a with disiamylborane¹⁰ followed by oxidation with NaOH- H_2O_2 cleanly produced 5.8 After

riences with allylcopper derivatives. (5) (a) Frangin, Y.; Favre, E.; Gaudemar, M. C. R. Hebd. Seances Acad.

Sci., Ser. C 1976, 282, 277. (b) Bernadou, F.; Miginiac, L. Tetrahedron Lett. 1976. 3083

(6) The following formal intramolecular allylzincation of an internal alkyne is known [Courtois, G.; Masson, A.; Miginiac, L. C. R. Hebd. Seances Acad. Sci., Ser. C 1978, 286, 265].



(7) Mikhailov, B. M. Organometal. Chem. Rev., Sect. A 1972, 8, 1.
(8) All isolated products have yielded IR as well as ¹H and ¹³C NMR

spectra consistent with the assigned structures. In addition, 2a, 3a, 4a, 4b, 4c, 6a, 8, and 10 have yielded satisfactory high-resolution MS spectra.

(9) The stereochemistry of the alkene products were established by NOE difference spectra experiments. In addition, the stereochemical assignments were supported by the ¹³C NMR spectra of the protonolysis products corre-sponding to **4a**, **4b**, and **4c**. Their doubly allylic carbon signals appear downfield by 5-10 ppm relative to their stereoisomers. (10) Brown, H. C. "Organic Synthesis via Boranes"; Wiley-Interscience:

New York, 1975.

(11) Our attempt to purify 5 by distillation led to a minor explosion. The crude product obtained after concentration was however sufficiently pure for the next step



concentration, it was further oxidized to $6a^8$ with chromic acid, the overall of **6a** from **4a** being 86%.¹⁰ Although direct treatment of 6a with 3 equiv of t-BuLi led to a mixture of products, its treatment first with 1 equiv of MeLi in ether at -78 °C then with 2 equiv of t-BuLi¹² in pentane at -78 °C cleanly produced 2a⁸ in 71% yield: bp 95 °C (0.1 mm); IR (neat) 1695 (s), 1585 (m), 1250 (s), 835 (s) cm⁻¹; ¹H NMR (CCl₄, C₆H₆) δ 0.1 (s, 9 H), $0.80 (t, J = 7 Hz, 3 H), 1.1-1.5 (m, 8 H), 2.0-2.5 (m, 6 H); {}^{13}C$ NMR (CDCl₃, Me₄Si) δ -0.32, 14.03, 22.58, 28.72, 29.54, 31.72, 32.82, 34.16, 35.82, 139.34, 189.62, 214.23. The favorable effect of an α -silyl group in α,β -unsaturated enones on the Michael reaction is well documented,¹² and our efforts to utilize 2 in the Michael and other related reactions are underway.

Conversion of 4a into 3a was achieved in one step as follows (eq 3). To a dry flask charged with $Pd(PPh_3)_4$ (1.16 g, 1.0 mmol)



and carbon monoxide (1.1 atm) were added at room temperature THF (5 mL), triethylamine (0.16 mL, 1.1 mmol), and 4a (0.35 g, 1.0 mmol). The reaction mixture was heated for 18-24 h at 60 °C under 1.1 atm of carbon monoxide, and was poured onto saturated aqueous ammonium chloride (10 mL). Extraction (ether), washing (aqueous NaCl), drying (MgSO₄), and chromatography (Florisil, CH₂Cl₂) gave 0.135 g (54%) of 3a: IR (neat) 1740 (m), 1690 (s), 1650 (m), 1575 (m), 1250 (m), 840 (s) cm⁻¹; ¹H NMR (CCl₄, Me₄Si) δ 0.15 (s, 9 H), 0.86 (t, 3 H), 1.1–1.6 (m, 8 H), 2.47 (t, J = 7 Hz, 2 H), 3.10 (s, 2 H) 5.20 (d, J = 1 Hz,1 H), 5.85 (d, J = 1 Hz, 1 H). Our attempts to achieve the same transformation with a catalytic amount of a Pd complex have so far been frustrated.

The mechanistic details of the reaction are yet to be clarified. However, a scheme shown in eq 4 correctly predicted the structure of the only cyclic product (3a).



The structural similarity between 3a and methylenomycin B¹³ (3b) prompted us to seek allylmetalation reactions of dialkylsubstituted internal alkynes. After unsuccessful attempts with allylmetals containing Al, B, Cu, Mg, and Ti, we turned our

⁽²⁾ For a recent review, see: Normant, J. F.; Alexakis, A. Synthesis 1981, 841

⁽³⁾ For a review of carboalumination of alkynes, see: Negishi, E. Pure Appl. Chem. 1981, 53, 2333. (4) Professor J. F. Normant has also informed us of their negative expe-

⁽¹²⁾ Jorgenson, M. J. Org. React. 1970, 18, 1.

^{(13) (}a) Stork, G.; Ganem, B. J. Am. Chem. Soc. 1973, 95, 6152. (b) Stork, G.; Singh, J. Ibid. 1974, 96, 6181.

⁽¹⁴⁾ For a recent synthesis of 3b, see: Billington, D. C.; Pauson, P. L. Organometallics 1982, 1, 1560.



attention to bimetallic systems and have found that treatment of 5-decyne with diallylzinc and I₂ZrCp₂,¹ generated in situ from Cl₂ZrCp₂ and NaI, smoothly provides, after iodinolysis, $4b^8 (Z/E)$ = $94/6)^{9}$ in 84% yield. Likewise, 2-butyne is converted into $4c^{8}$ $(Z/E = 80/20)^9$ in 92% yield. As expected, conversion of 4c into methylenomycin B (3b) proceeds in 51% yield under the same reaction conditions as those for the preparation of 3a: bp 60 °C (0.1 mm); IR (neat) 1690 (s), 1665 (m), 1630 (s), 1330 (s), 1030 (s), 930 (m), 800 (m) cm⁻¹; ¹H NMR (CDCl₃, Me₄Si) δ 1.74 (s, 3 H), 2.05 (s, 3 H), 3.05 (bs, 2 H), 5.30 (d, J = 1 Hz, 1 H), 6.00 (d, J = 1 Hz, 1 H); ¹³C NMR (CDCl₃, Me₄Si) δ 8.23, 16.64, 36.97, 114.85, 138.23, 141.78, 164.02, 196.04.

The necessity for I₂ZrCp₂ in the above allylmetalation suggested to us that, unlike the known allylmetalation reactions that are believed to proceed via six-centered transition states 7, this reaction might proceed via a four-centered transition state, as might be suggested for the previously reported Zr-promoted carbometalation reactions.^{1,3} To probe this point, the regioselectivity of the two allylzincation reactions herein reported were examined. The reaction of 1-(trimethylsilyl)-1-octyne with crotylzinc chloride, generated in situ by treatment of crotylmagnesium chloride with ZnCl₂, followed by protonolysis produced $\hat{\mathbf{8}}^8$ (E/Z = 90/10)⁹ in



68% yield with no indication for the formation of its regioisomer 9. On the other hand, the reaction of 5-decyne with dicrotylzinc in the presence of I_2ZrCp_2 , generated as described earlier, followed by protonolysis gave 10^8 in 92% yield as an essentially single isomer, with no indication for the formation of its regioisomer 11. These two reactions must proceed via different paths, and the results are consistent with the notion that the former may proceed via 7, while the latter may involve a four-centered transition state. Our attempts to react 1-(trimethylsilyl)-1-octyne with either isoprenylzinc chloride or diisoprenylzinc did not produce cleanly the desired products.

The results described herein not only expand the scope of controlled carbometalation of alkynes but also demonstrate a novel and potentially attactive approach to the synthesis of carbocycles via carbometalation.

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Supplementary Material Available: Experimental findings for 4a-c, 5, 6a, 8, and 10 (2 pages). Ordering information is given on any current masthead page.

Synthesis and Molecular Structures of Homoleptic Dicyclohexylphosphide Complexes of the Early **Transition Metals**

R. T. Baker,* P. J. Krusic, T. H. Tulip, J. C. Calabrese, and S. S. Wreford

> Contribution No. 3292 Central Research & Development Department Experimental Station E. I. du Pont de Nemours and Company, Inc. Wilmington, Delaware 19898

> > Received July 21, 1983

We report the isolation of homoleptic dicyclohexylphosphide complexes, $M_x(PCy_2)_y$, for 10 of the 12 early transition metals. These are the first well-characterized examples 1-4,20 of a potentially large class of compounds, analogous to the well-known⁵ diorganoamide complexes $M_x(NR_2)_y$. The unusual structures of the new complexes result from the bulky PCy_2 ligand, metalphosphorus multiple bonding, and, for the anionic derivatives, strong phosphorus-lithium interactions.

Addition of a tetrahydrofuran (THF) solution of LiPCy26 to a solution or suspension of a transition-metal halide THF adduct⁷ at -80 °C⁸ produces the complexes 1-10 (Table I, supplementary material). 1-9 are isolated as crystalline solids by hexane extraction of the evaporated reaction residue, addition of 1,2-dimethoxyethane (DME), and cooling to -30 °C. Complex 10 is insoluble in hexane or benzene and is separated from LiBr by fractional crystallization from DME at -30 °C. Four classes of compounds are distinguishable:

 $[Li(DME)][M(PCy_2)_5]$ (1, M = Zr; 2, M = Hf). The molecular structure of 2.C6H6 in Figure 1A was determined by X-ray diffraction.9 The distorted trigonal-bipyramidal geometry about hafnium has Hf-P bond distances^{10,11} and phosphorus geometries¹² consistent with the valence bond representation shown. An 18-e⁻ configuration is attained by participation of the P(4) lone pair in a three-center, two-electron Hf-P-Li bond. The tight binding

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(4) Monomeric THF adducts of tris(di-tert-butylphosphide) complexes of several lanthanides have been reported: Schumann, H.; Frisch, G.-M. Z. Naturforsch. 1979, 34b, 748-749

(5) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Ellis Horwood: Chichester, 1980; Chapter 8.

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(6) Isolated as a yellow solid from n-BuLi and HPCy₂ in diethyl ether.
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(8) Low-temperature, dropwise addition suppresses reduction of the transition metal with concomitant formation of P_2Cy_4 .

(9) Crystal data for 2-C₆H₆ grown from benzene-DME: $C_{70}H_{126}HfLi-O_2P_5$, $M_r = 1340.08$, monoclinic, space group $P2_1/n$ (No. 14), a = 19.215 (2) Å, b = 19.922 (3) Å, c = 18.821 (2) Å, $\beta = 90.171$ (1)°, V = 7205 (3) Å³, Z = 4, ρ (calcd) = 1.24 g cm⁻¹; T = -100 °C. On the basis of refinement of 677 variables (Hf, P, O, and non-benzene C's with anisotropic thermal parameters) using 7971 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, R = 0.036, R_w = 0.038. Full details will be published separately (see also supplementary material)

(10) Relevant bond distances: Hf-P(1) = 2.533(1), Hf-P(2) = 2.475(1),(10) Relevant on a distances. In $\Gamma(1) = 2.555$ (1), In $\Gamma(2) = 2.475$ (1), Hf-P(3) = 2.504 (1), Hf-P(4) = 2.639 (1), Hf-P(5) = 2.712 (1), P(4)-Li = 2.653 (8), P(5)-Li = 2.579 (8) Å. (11) Cf. Hf-P = 2.682 (1), Hf = P = 2.488 (1) Å in $(\eta$ -C₅H₅)₂Hf(PEt₂)₂: Baker, R. T.; Whitney, J. F.; Wreford, S. S. Organometallics **1983**, 2,

1049-1051

(12) Displacement of Hf atom from the PC₂ plane: P(1) = 0.634, P(2) = 0.095, P(3) = 0.647, P(4) = 1.185, P(5) = 2.058 Å.

⁽¹⁵⁾ Note Added in Proof: Professor G. Molander of the University of Colorado has informed us of their study of allylmetalation of alkynylsilanes.

⁽¹⁾ Early reports by Issleib, et al., include the reactions of LiPCy₂ with $MCl_3 \cdot 3THF$ (M = Ti, V, Cr)² and $MnBr_2^3$; the products are misformulated (2) Issleib, K.; Wenschuh, E. Chem. Ber. 1964, 97, 715-720.