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 eV).

At sufficiently low pH values[12] 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 $k_Q = (4.9 \pm 0.8) \times 10^8$ M^{-1} s^{-1}. Proton-transfer quenching has also been observed with the aminonaphthalenes[16] 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

Table I. Ground- and Excited-State Acidities

system	pK_a	pK_a^*
1-(*p*-aminophenyl)pyrene	4.05	
by Forster cycle		3.3
by fluorescence titration		3.6
aniline	4.58[a]	
1-aminopyrene	2.8[b]	−1.2[c]
1-aminonaphthalene	3.9[d]	−1.0[d]
2-aminonaphthalene	4.1[d]	−0.8[d]

[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

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

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

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

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

(10) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.
(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 localized π,π^* state.
(12) The "pH" values, obtained with a Markson S-585 semimicro combination 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_a 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, $\gamma_{\pm}$ 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 $[H^+](\gamma_{\pm})^{-2Z_j}$, where Z_j is the charge on the species being quenched, because of the influence of the ionic environment. The dependence on $\gamma_{\pm}^2$ in our system may reflect an interaction between the proton quencher and the pyrene radical anion moiety of the CT state ($Z_j = -1$).
(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.

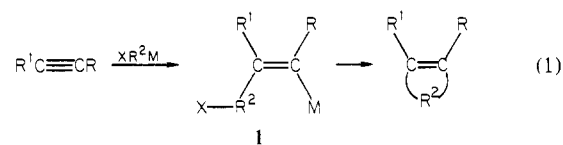# Novel Syntheses of α,β-Unsaturated Cyclopentenones via Allylzincation of Alkynes[1]

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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

(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-

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6

3

$$R'C{\equiv}CR + \underset{}{\diagup\!\!\!\diagdown\!\!\!\diagup M} \quad (2)$$
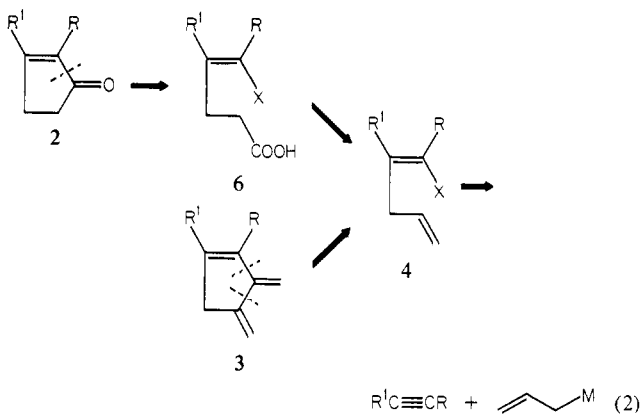
lylmetalation of alkynes in the literature was surprisingly limited.[2] Aluminum[3] and copper,[2] two metals that have been most widely used for carbometalation of alkynes, do not readily undergo allylmetalation. In fact, all our attempts at observing their allylmetalation have failed.[4] Although allylzincation 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 alkynes[7] appears to be the only allylmetalation in the literature that gives single-stage 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-1,4-pentadiene[8] (**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 ^{1}H and ^{13}C 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 Me$_3$Si group plays a critical role in inducing the observed carbometalation. Hydroboration of **4a** with disiamylborane[10] followed by oxidation with NaOH–H$_2$O$_2$ cleanly produced **5**.[8] After

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(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 experiences 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].

$$MeC{\equiv}C(CH_2)_3CH{=}CHCH_2Br \xrightarrow[2\ -\text{H}_3\text{O}^+]{1\ Z_n}$$
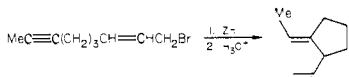
(7) Mikhailov, B. M. *Organometal. Chem. Rev., Sect. A* **1972**, *8*, 1.

(8) All isolated products have yielded IR as well as ^{1}H and ^{13}C 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 ^{13}C NMR spectra of the protonolysis products corresponding 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.


4a   **5**   **6a**

2a
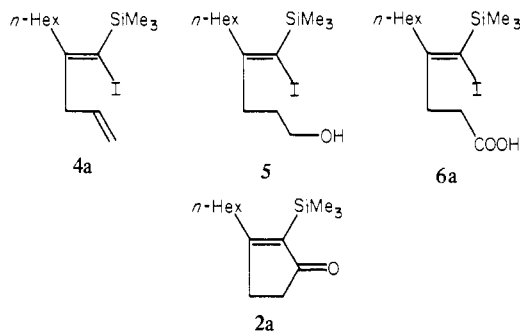
concentration, it was further oxidized to **6a**[8] with chromic acid, the overall of **6a** from **4a** being 86%.[10] Although direct treatment of **6a** with 3 equiv of *t*-BuLi led to a mixture of products, its treatment first with 1 equiv of MeLi in ether at –78 °C then with 2 equiv of *t*-BuLi[12] in pentane at –78 °C cleanly produced **2a**[8] in 71% yield: bp 95 °C (0.1 mm); IR (neat) 1695 (s), 1585 (m), 1250 (s), 835 (s) cm^{-1}; ^{1}H NMR (CCl$_4$, C$_6$H$_6$) 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 (CDCl$_3$, Me$_4$Si) 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)

$$\quad (3)$$

4a   **3a**
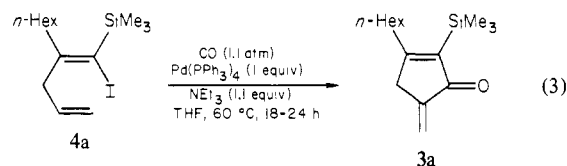
and carbon monoxide (1.1 atm) were added at room temperature THF (5 mL), triethylamine (0.16 mL, 1.1 mmol), and **4a** (0.35 g, 1.0 mmol). The reaction mixture was heated for 18–24 h at 60 °C under 1.1 atm of carbon monoxide, and was poured onto saturated aqueous ammonium chloride (10 mL). Extraction (ether), washing (aqueous NaCl), drying (MgSO$_4$), and chromatography (Florisil, CH$_2$Cl$_2$) gave 0.135 g (54%) of **3a**: IR (neat) 1740 (m), 1690 (s), 1650 (m), 1575 (m), 1250 (m), 840 (s) cm^{-1}; ^{1}H NMR (CCl$_4$, Me$_4$Si) 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**).


$$\quad (4)$$
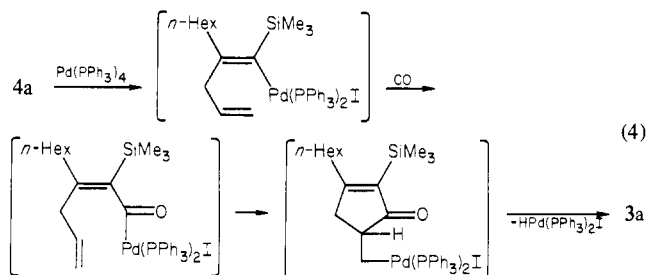
The structural similarity between **3a** and methylenomycin B[13] (**3b**) prompted us to seek allylmetalation reactions of dialkyl-substituted internal alkynes. After unsuccessful attempts with allylmetals containing Al, B, Cu, Mg, and Ti, we turned our

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(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.

4b   4c   3b   7
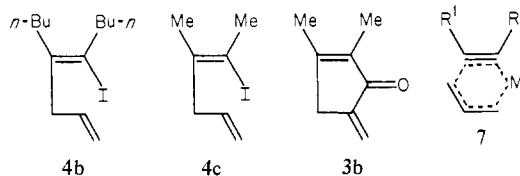
attention to bimetallic systems and have found that treatment of 5-decyne with diallylzinc and I_2ZrCp_2,[1] generated in situ from Cl_2ZrCp_2 and NaI, smoothly provides, after iodinolysis, **4b**[8] (Z/E = 94/6)[9] in 84% yield. Likewise, 2-butyne is converted into **4c**[8] (Z/E = 80/20)[9] in 92% 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 (CDCl$_3$, Me$_4$Si) 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); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 8.23, 16.64, 36.97, 114.85, 138.23, 141.78, 164.02, 196.04.

The necessity for I_2ZrCp_2 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 ZnCl$_2$, followed by protonolysis produced **8**[8] (E/Z = 90/10)[9] in

8   9   10

11
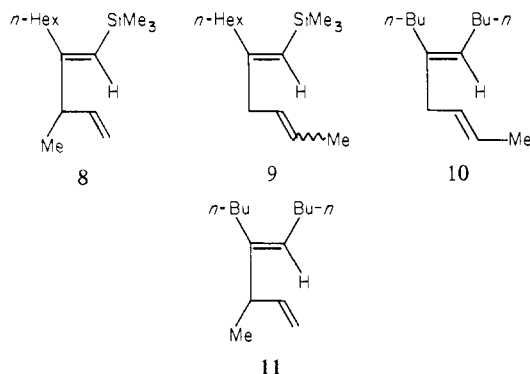
68% yield with no indication for the formation of its regioisomer **9**. On the other hand, the reaction of 5-decyne with dicrotylzinc in the presence of I_2ZrCp_2, generated as described earlier, followed by protonolysis gave **10**[8] in 92% yield as an essentially single isomer, with no indication 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.

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

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

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

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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-known[5] diorganoamide complexes $M_x(NR_2)_y$. The unusual structures of the new complexes result from the bulky PCy_2 ligand, metal-phosphorus multiple bonding, and, for the anionic derivatives, strong phosphorus–lithium interactions.

Addition of a tetrahydrofuran (THF) solution of LiPCy$_2$[6] to a solution or suspension of a transition-metal halide THF adduct[7] at −80 °C[8] 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**·C$_6$H$_6$ 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 geometries[12] 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

(1) Early reports by Issleib, et al., include the reactions of LiPCy$_2$ with MCl$_3$·3THF (M = Ti, V, Cr)[2] and MnBr$_2$[3]; the products are misformulated as monomeric TiP$_3$, VP$_3$, CrP$_3$, and Li[MnP$_3$] species, where P = PCy$_2$.

(2) Issleib, K.; Wenschuh, E. *Chem. Ber.* **1964**, *97*, 715–720.

(3) Issleib, K.; Wenschuh, E.; Frohlich, H.-O. *Z. Naturforsch.* **1962**, *17b*, 778–779.

(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.

(6) Isolated as a yellow solid from *n*-BuLi and HPCy$_2$ in diethyl ether. Modified after: Issleib, K.; Tzschach, A. *Chem. Ber.* **1959**, *92*, 1118–1126.

(7) M = Ti, Zr, Hf, V, Nb: Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135–139. M = Cr: Herwig, W.; Zeiss, H. H. *J. Org. Chem.* **1958**, *23*, 1404. M = Mo: Dilworth, J. R.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1983**, 397–398. M = W: Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430–1431. M = Mn: Hosseiny, A.; McAuliffe, C. A.; Minten, K.; Parrott, M. J.; Pritchard, R.; James, J. *Inorg. Chim. Acta* **1980**, *39*, 227–231. M = Re: Allen, E. A.; Johnson, N. P.; Rosevear, D. T.; Wilkinson, W. *J. Chem. Soc. A* **1969**, 788–791.

(8) Low-temperature, dropwise addition suppresses reduction of the transition metal with concomitant formation of P_2Cy_4.

(9) Crystal data for **2**·C$_6$H$_6$ grown from benzene-DME: C$_{70}$H$_{126}$HfLiO$_2$P$_5$, 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, β = 90.171 (1)°, V = 7205 (3) Å^3, 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), 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 $\rightleftharpoons$ P = 2.488 (1) Å in (η-C$_5$H$_5$)$_2$Hf(PEt$_2$)$_2$: Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049–1051.

(12) Displacement of Hf atom from the PC$_2$ plane: P(1) = 0.634, P(2) = 0.095, P(3) = 0.647, P(4) = 1.185, P(5) = 2.058 Å.