Reactivity Patterns for μ-η^1:η^2-Allenyl Complexes. A Novel Synthetic Route to Dimetallacyclopentanes and Dimetallacyclopentenes via Regiospecific Additions of Carbon, Nitrogen, and Phosphorus Nucleophiles to $Ru_2(CO)_6(\mu\text{-}\eta^1{:}\eta^2\text{-}PhC{=}C{=}CH_2)(\mu\text{-}PPh_2)$

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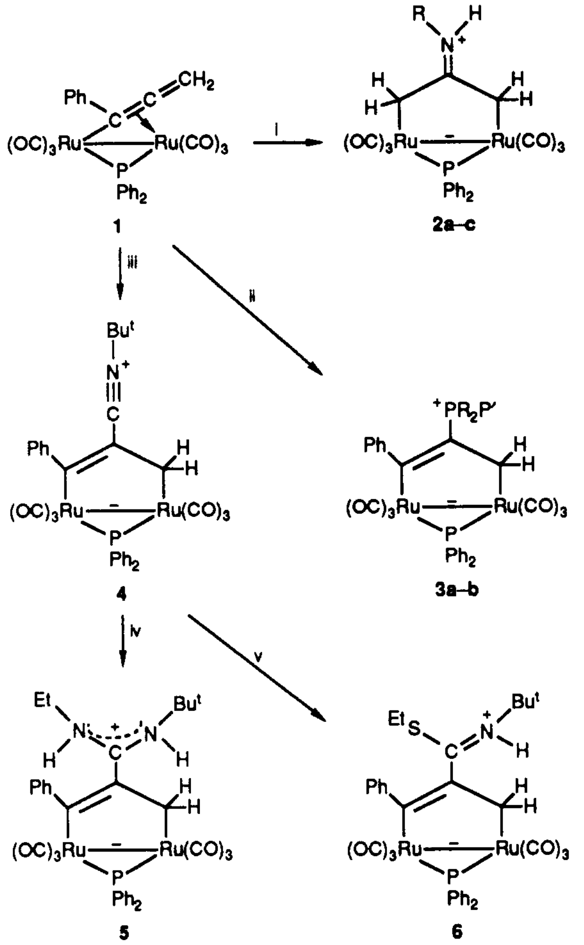
Summary: Reaction of the bimetallic allenyl complex $Ru_2(CO)_6(\mu\text{-}\eta^1{:}\eta^2\text{-}PhC{=}C{=}CH_2)(\mu\text{-}PPh_2)$ (**1**) with H_2NR (R = Et, *n*-Pr, Cy), PR_2R' (R = Cy, R′ = H; R = R′ = OEt), or *t*-BuNC results in exclusive attack at the β-carbon atom, forming the novel zwitterionic dimetallacyclopentane and dimetallacyclopentene derivatives $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^1\text{-}PhHC{-}C(HNR){-}CH_2](\mu\text{-}PPh_2)$ (**2a**–**c**), $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^1\text{-}PhC{=}C(PR_2R'){-}CH_2](\mu\text{-}PPh_2)$ (**3a**,**b**), and $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^1\text{-}PhC{=}C(CN\text{-}t\text{-}Bu)CH_2](\mu\text{-}PPh_2)$ (**4**). The isonitrile adduct reacts smoothly with either H_2NEt or EtSH to give $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^1\text{-}PhC{=}C\{C(EtNH)N(H\text{-}t\text{-}Bu)\}{-}CH_2](\mu\text{-}PPh_2)$ (**5**) or $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^1\text{-}PhC{=}C\{C(EtS)N(H\text{-}t\text{-}Bu)\}{-}CH_2](\mu\text{-}PPh_2)$ (**6**). Compounds **2a**, **3a**, and **5** have been structurally characterized by single-crystal X-ray analysis. EHMO calculations indicate that the observed reactivity is under charge and orbital control.

Scheme I[a]



[a] Reagents and conditions: (i) excess H_2NR (R = Et, *n*-Pr, Cy), in toluene, 25 °C, 24 h, 70–80%; (ii) 3 equiv of PR_2R' (R = Cy, R′ = H; R = R′ = OEt), in heptane, 2 °C, 12 h, 88%; (iii) 1.2 equiv of *t*-BuNC, in toluene, 10 °C, 4 h, 95%; (iv) excess H_2NEt, in toluene/CH_2Cl_2, 25 °C, 2 h, 82%; (v) excess EtSH, in toluene/CH_2Cl_2, 25 °C, 2 h, 75%.

As a polyunsaturated C_3 fragment isomeric with the propynyl group ($-C{\equiv}C{-}CH_3$), the allenyl ligand ($-CH{=}C{=}CH_2$) should have an extensive organometallic chemistry. Surprisingly, the chemical reactivity of bi- and polynuclear allenyl complexes[1] has largely escaped attention, despite the fact that other unsaturated hydrocarbyl ligands, including some with cumulated multiple bonds,[2] have been the focus of considerable research.[3] The recent development of synthetic routes to bi- and trinuclear allenyl complexes[4a–f] allows a systematic examination of reaction chemistry, and in this communication we describe the generation of novel five-membered dimetallacycles via nucleophilic additions to the binuclear allenyl complex $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^2\text{-}C(Ph){=}C{=}CH_2](\mu\text{-}PPh_2)$ (1). Although

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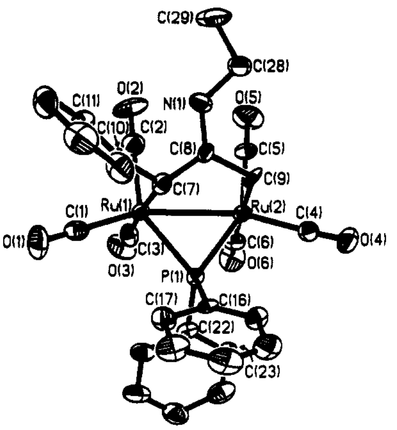

Figure 1. Molecular plot of the structure of molecule A of $Ru_2(CO)_6[\mu\text{-}\eta^1\text{:}\eta^1\text{-PhHC—C(HNEt)—CH}_2](\mu\text{-PPh}_2)$ (**2a**). Selected bond lengths (Å) and bond angles (deg) for molecule A, one of two independent but chemically indistinguishable molecules in the asymmetric unit, are as follows: Ru(1)-Ru(2) = 2.872 (1), Ru(1)-C(7) = 2.255 (8), Ru(2)-C(9) = 2.239 (8), C(7)-C(8) = 1.441 (13), C(8)-C(9) = 1.447 (12), C(8)-N(1) = 1.314 (11); Ru(1)-P(1)-Ru(2) = 75.7 (1), Ru(2)-Ru(1)-C(7) = 85.6 (2), Ru(1)-C(7)-C(8) = 101.1 (5), C(7)-C(8)-C(9) = 120.0 (8), C(9)-Ru(2)-Ru(1) = 84.6 (2), P(1)-Ru(1)-C(7) = 86.4 (2).

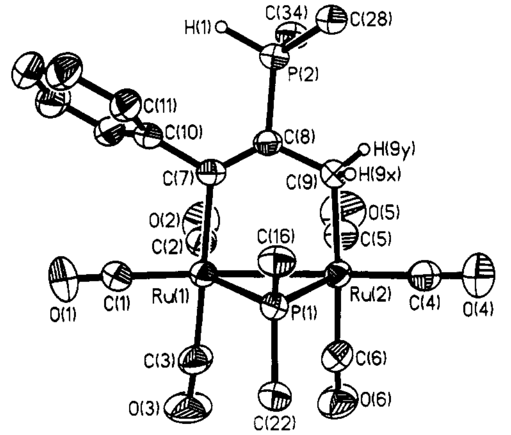

Figure 2. Molecular plot of $Ru_2(CO)_6[\mu\text{-}\eta^1\text{:}\eta^1\text{-PhC=C(PCy}_2\text{H)—CH}_2](\mu\text{-PPh}_2)$ (**3a**). Important bond lengths (Å) and bond angles (deg) include the following: Ru(1)-Ru(2) = 2.851 (1), Ru(1)-C(7) = 2.169 (3), Ru(2)-C(9) = 2.204 (3), C(7)-C(8) = 1.336 (4), C(8)-C(9) = 1.510 (5), C(8)-P(2) = 1.808 (3); Ru(1)-P(1)-Ru(2) = 75.7 (1), Ru(2)-Ru(1)-C(7) = 85.9 (1), Ru(1)-C(7)-C(8) = 121.9 (2), C(7)-C(8)-C(9) = 127.7 (3), C(9)-Ru(2)-Ru(1) = 86.1 (1), P(1)-Ru(1)-C(7) = 91.3 (1).

a few dimetallacyclopentanes and dimetallacyclopentenones are known,[5] the present route, involving regiospecific nucleophilic attack at C_β of **1** by neutral carbon, nitrogen, and phosphorus nucleophiles, is attractive because of its simplicity, high yields, and potential generality.

Polynuclear allenyl complexes are accessible via (i) diazoalkane additions to acetylides,[4a-c] (ii) reactions of propargyl halides with metal carbonyl anions,[4d,e] (iii) reactions of propargyl organometallics with metal carbo-

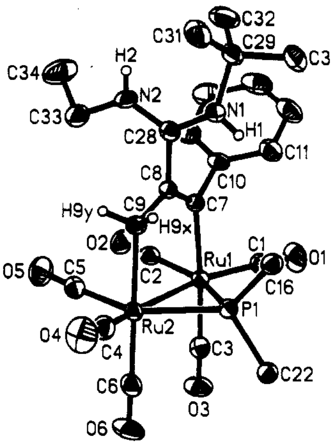

Figure 3. Molecular plot of $Ru_2(CO)_6[\mu\text{-}\eta^1\text{:}\eta^1\text{-PhC=C\{C(EtNH)N(H)(}t\text{-Bu)\}—CH}_2](\mu\text{-PPh}_2)$ (**5**). Selected bond lengths (Å) and bond angles (deg) are as follows: Ru(1)-Ru(2) = 2.869 (1), Ru(1)-C(7) = 2.154 (3), Ru(2)-C(9) = 2.197 (3), C(7)-C(8) = 1.342 (4), C(8)-C(9) = 1.505 (5), C(8)-C(28) = 1.501 (4), C(28)-N(1) = 1.315 (5), C(28)-N(2) = 1.326 (4), N(1)-C(29) = 1.497, N(2)-C(33) = 1.462 (6); Ru(1)-P(1)-Ru(2) = 75.9 (1), Ru(2)-Ru(1)-C(7) = 85.1 (1), Ru(1)-C(7)-C(8) = 123.2 (2), C(7)-C(8)-C(9) = 128.6 (3), C(9)-Ru(2)-Ru(1) = 86.9 (1), P(1)-Ru(1)-C(7) = 87.1 (1), C(8)-C(28)-N(1) = 116.9 (3), C(8)-C(28)-N(2) = 120.7 (3), N(1)-C(28)-N(2) = 122.3 (3).

nyls,[4f,k] or (iv) reactions of $M_3(CO)_{12}$ (M = Ru, Os) or $H_2Os_3(CO)_{10}$ with specific alkenes, dienes, and alkynes.[4g-j] We have explored in detail the chemistry of **1** in an effort to evaluate the reactivity of the coordinated [C_β and C_α(R)] and uncoordinated ($C_\gamma H_2$) sites of the ligand.

As shown in Scheme I, treatment of **1**[4a] (0.20 g, 0.3 mmol) in toluene with an excess of amine gave, after removal of excess amine and crystallization of the residue from toluene, yellow crystals of $Ru_2(CO)_6[\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph(H)-C—C(NHR)—CH}_2](\mu\text{-PPh}_2)$ (**2a**, R = Et; **2b**, R = *n*-Pr; **2c**, R = Cy) in high yields.[6] Similarly, addition of 3 equiv

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[6] Selected spectroscopic data for complexes **2a–c** are as follows. Compound **2a**: IR (C_7H_{16}) ν(CO) 2062 (s), 2029 (vs), 1991 (s), 1979 (s), 1972 (m), 1957 (vw) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$; 81.0 MHz; 298 K) δ 155.5 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$; 50.3 MHz; 298 K) δ 206.9 (d, CO, $^2J_{PC}$ = 59.7 Hz), 203.0 (d, CO, $^2J_{PC}$ = 61.1 Hz), 197.8 (d, CO, $^2J_{PC}$ = 10.9 Hz), 197.4 (s, CO), 197.3 (d, CO, $^2J_{PC}$ = 11.3 Hz), 196.5 (s, CO), 194.0 (s, C_β), 145.5–125.2 (m, *C*Ph), 38.3 (s, N–*C*H_2), 33.4 (s, C_α), 14.1 (s, *C*H_3), 0.4 (d, C_γ, $^2J_{PC}$ = 5.0 Hz); ^1H NMR ($CDCl_3$; 250.1 MHz; 298 K) δ 7.96–6.83 (m, Ph*H*), 5.81 (br s, N–*H*), 3.37 (ddq, CH_2CH_3, $^3J_{HCH_3}$ = 7.2 Hz, $^3J_{HNH}$ = 7.2 Hz, $^2J_{HH}$ = 13.0 Hz), 3.13 (ddq, CH_2CH_3, $^3J_{HCH_3}$ = 7.2 Hz, $^3J_{HNH}$ = 7.2 Hz, $^2J_{HH}$ = 13.0 Hz), 2.89 (d, C_α–*H*, $^3J_{PH}$ = 6.2 Hz), 1.54 (s, $C_\gamma H_2$), 1.10 (t, CH_3, $^3J_{HH}$ = 7.2 Hz). Anal. Calcd for $C_{29}H_{24}NO_6PRu_2$: C, 48.67; H, 3.38; N, 1.96; P, 4.33. Found: C, 48.83, H, 3.53; N, 2.05; P, 4.06. Compound **2b**: IR (C_7H_{16}) ν(CO) 2062 (s), 2029 (vs), 1991 (s), 1979 (s), 1972 (m), 1957 (vw) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$; 81.0 MHz; 298 K) δ 155.6 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$; 50.3 MHz; 298 K) δ 206.9 (d, CO, $^2J_{PC}$ = 59.5 Hz), 203.1 (d, CO, $^2J_{PC}$ = 61.0 Hz); 197.9 (d, CO, $^2J_{PC}$ = 10.8 Hz), 197.5 (s, CO), 197.4 (d, CO, $^2J_{PC}$ = 9.2 Hz), 196.7 (d, CO, $^2J_{PC}$ = 3.1 Hz), 194.2 (s, C_β), 145.6–125.3 (m, *C*Ph), 45.1 (s, N–*C*H_2–), 33.6 (d, C_α, $^2J_{PC}$ = 3.8 Hz), 22.3 (s, –CH_2–*C*H_2–CH_3), 11.0 (s, *C*H_3), 0.44 (d, C_γ, $^2J_{PC}$ = 5.5 Hz); ^1H NMR ($CDCl_3$; 250.1 MHz; 298 K) δ 7.94–6.70 (m, Ph*H*), 5.88 (br s, N–*H*), 3.27 (ddt, N–C*H*$_2$, $^3J_{HCH_2}$ = 7.3 Hz, $^3J_{HNH}$ = 7.3 Hz, $^2J_{HH}$ = 12.8 Hz), 3.07 (ddt, N–C*H*$_2$, $^3J_{HCH_2}$ = 7.3 Hz, $^3J_{HNH}$ = 7.3 Hz, $^2J_{HH}$ = 12.8 Hz), 2.90 (d, C_α–H, $^3J_{PH}$ = 6.2 Hz), 1.54 (s, $C_\gamma H_2$), 1.43 (m, CH_2–C*H*$_2$–CH_3), 0.81 (t, C*H*$_3$, $^3J_{HH}$ = 7.3 Hz). Anal. Calcd for $C_{30}H_{26}NO_6PRu_2$: C, 49.38; H, 3.59; N, 1.92; P, 4.25. Found: C, 49.44; H, 3.66; N, 2.03; P, 4.09. Compound **2c**: IR (C_7H_{16}) ν(CO) 2061 (s), 2028 (vs), 1990 (s), 1978 (s), 1971 (m), 1957 (vw) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$; 81.0 MHz; 298 K) δ 155.8 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$; 50.3 MHz; 298 K) δ 207.2 (d, CO, $^2J_{PC}$ = 59.6 Hz), 203.4 (d, CO, $^2J_{PC}$ = 61.6 Hz), 197.9 (d, CO, $^2J_{PC}$ = 11.3 Hz), 197.6 (d, CO, $^2J_{PC}$ = 3.5 Hz), 197.3 (d, CO, $^2J_{PC}$ = 11.1 Hz), 196.7 (d, CO, $^2J_{PC}$ = 3.4 Hz), 193.6 (s, C_β), 145.6–125.2 (m, *C*–Ph), 52.0 (s, Cy–*C*–N), 33.5 (d, C_α, $^2J_{PC}$ = 3.9 Hz), 33.4 (s, Cy *C*H_2), 32.4 (s, Cy *C*′H_2), 25.0 (s, Cy *C*″H_2), 24.3 (s, Cy *C*‴H_2), 24.0 (s, Cy *C*⁗H_2), 0.6 (d, C_γ, $^2J_{PC}$ = 5.3 Hz); ^1H NMR ($CDCl_3$; 250.1 MHz; 298 K) δ 7.95–6.97 (m, Ph *H*), 5.92 (d, N–*H*, $^3J_{HH}$ = 8.5 Hz), 3.42 (m, N–C–*H*), 2.86 (d, C_α–*H*, $^3J_{PH}$ = 6.1 Hz), 2.14–0.74 (m, C_γ*H*$_2$ and Cy C*H*$_2$). Anal. Calcd for $C_{33}H_{30}NO_6PRu_2\cdot0.5C_7H_8$: C, 53.74; H, 4.20. Found: C, 53.56; H, 4.60.

of phosphine or phosphite to **1** afforded essentially quantitative yields of $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^1\text{-}PhC{=}C(PR_2R')\text{—}CH_2](\mu\text{-}PPh_2)$ (**3a**, R = Cy, R′ = H; **3b**, R = R′ = OEt).[7]

In a remarkably facile carbon–carbon bond-forming reaction **1** reacted with a slight excess of *t*-BuNC at 10 °C to afford the product of nucleophilic attack of the isonitrile at C_β, compound **4**,[8] quantitatively.

With excess primary amine, **4**[8] (0.22 g, 0.29 mmol) gave, after recrystallization from $EtOH/CH_2Cl_2/C_7H_{16}$, yellow crystals of $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^1\text{-}PhC{=}C\{C(EtNH)N(H)(t\text{-}Bu)\}\text{—}CH_2](\mu\text{-}PPh_2)$ (**5**), the product of N–H addition across the C–N multiple bond of the "carbon coordinated" isonitrile.[9] Addition of excess thiol to **4** likewise generated the thioamidinium derivative $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^1\text{-}PhC{=}C\text{-}\{C(EtS)N(H)(t\text{-}Bu)\}\text{—}CH_2](\mu\text{-}PPh_2)$ (**6**).[10]

The structures of complexes **2a**, **3a**, and **5** have been determined by single-crystal X-ray diffraction.[11] Molecular plots are depicted in Figures 1–3, with pertinent bond lengths and angles. Amines react with proton transfer across the $C_\alpha{=}C_\beta$ double bond, generating zwitterionic dimetallacyclopentane derivatives, whereas the phosphorus and isocyanide nucleophiles give dimetallacyclopentenes. The formulation of **2a** as an imine derivative of a 1,2-dimetallacyclopentan-4-one was confirmed by the C(8)–N(1) bond distance (1.314 (11) Å) and by the planarity at C(8) and N(1). The C(7)–C(8) bond length (1.441 (13) Å) is typical of a C(sp³)–C(sp²) bond, in contrast to the case for **3a**, where the C(7)–C(8) bond (1.336 (4) Å) is olefinic. In **3a** and **5**, the five-membered ring is remarkably planar and oriented essentially 90° to the phosphido bridge. In complex **5**, the N–C–N system is delocalized, being allylic in nature, with C–N bond lengths of C(28)–N(1) = 1.315 (5) Å and C(28)–N(2) = 1.326 (4) Å. The formation of complexes **2a–c** and **3a**,**b** represent facile C–N and C–P bond-forming processes. Conversion of **1** to **4** and **5** generates C–C and C–N bonds in a remarkably simple two-step process. In all of the zwitterions **2–6**, ν(CO) IR frequencies are lower than in **1**, indicating that the negative charge is partially delocalized onto the $Ru_2(CO)_6(\mu\text{-}PPh_2)$ framework.

The regioselectivity of attack at C_β in **1** with carbon, nitrogen, and phosphorus nucleophiles contrasts sharply with results from trinuclear $\mu_3\text{-}\eta^3$-allenyl systems where reactivity at the metal centers[1d] or at $C_\gamma H_2$[1b,c] has been reported. EHMO calculations[12] show that while in the ground state of a model for **1**, $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^2\text{-}C_\alpha(H){=}C_\beta{=}C_\gamma H_2](\mu\text{-}PH_2)$, with parameters derived from the X-ray structure of $Ru_2(CO)_6[\mu\text{-}\eta^1{:}\eta^2\text{-}C(Ph){=}C{=}C(Ph)_2](\mu\text{-}PPh_2)$,[4a] the LUMO has a component centered on C_α, this carbon atom in **1** is sterically inaccessible. However, as the methylene unit rotates about the C_β–C_γ bond, a process responsible in part for the dynamic behavior of **1**,[4a] the orbital contribution to the LUMO from

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(7) Selected spectroscopic data for complexes **3a**,**b** are as follows. Compound **3a**: IR ($CHCl_3$) ν(CO) 2077 (w), 2051 (vs), 2014 (vs), 1981 (s), 1959 (m), 1934 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2; 101.3 MHz; 298 K) δ 180.1 (s, *P*Ph$_2$), 3.1 (s, *P*Cy$_2$H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2; 50.3 MHz; 298 K) δ 211.5 (d, CO, $^2J_{PC}$ = 50.6 Hz), 210.9 (d, CO, $^2J_{PC}$ = 58.2 Hz), 199.5 (s, CO), 198.7 (dd, CO, $^2J_{PC}$ = 9.8 Hz, $^4J_{PC}$ = 5.4 Hz), 197.6 (s, CO), 197.5 (dd, CO, $^2J_{PC}$ = 12.2 Hz, $^4J_{PC}$ = 4.8 Hz), 193.8 (d, C_β, $^1J_{PC}$ = 9.1 Hz), 157.2–122.7 (m, *C* Ph), 121.3 (dd, C_α, $^2J_{PC}$ = 26.1 Hz, $^2J_{P'C}$ = 13.1 Hz), 32.3–23.1 (m, Cy *C*), 7.7 (t, C_γ, $^2J_{PC} \approx {}^2J_{P'C} \approx$ 9.2 Hz); ^1H NMR (CD_2Cl_2; 250.1 MHz; 298 K) δ 7.93–6.35 (m, Ph *H*), 4.34 (dt, P–*H*, $^1J_{PH}$ = 435.2 Hz, $^3J_{HH}$ = 6.7 Hz), 2.08–0.70 (m, $C_\gamma H_2$ and Cy CH_2). Anal. Calcd for $C_{39}H_{40}O_6P_2Ru_2$: C, 53.91; H, 4.64; P, 7.13. Found: C, 54.03; H, 4.69; P, 7.29. Compound **3b**: IR ($CHCl_3$) ν(CO) 2077 (w), 2052 (vs), 2014 (vs), 1982 (s), 1961 (m), 1936 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$; 101.3 MHz; 298 K) δ 176.0 (s, *P*Ph$_2$), 25.3 [s, *P*(OEt)$_3$]; $^{13}C\{^1H\}$ NMR ($CDCl_3$; 50.3 MHz; 298 K) δ 211.0 (dd, CO, $^2J_{PC}$ = 50.1 Hz, $^4J_{PC}$ = 2.1 Hz), 210.2 (d, CO, $^2J_{PC}$ = 58.9 Hz), 207.4 (d, C_β, $^1J_{PC}$ = 8.6 Hz), 198.9 (s, CO), 198.0 (t, $^2J_{PC}$ = 9.5 Hz, $^4J_{PC}$ = 9.5 Hz), 197.5 (dd, CO, $^2J_{PC}$ = 12.5 Hz, $^4J_{PC}$ = 5.0 Hz), 197.0 (s, CO), 157.5–124.0 (m, *C* Ph), 122.7 (dd, C_α, $^2J_{PC}$ = 92.4 Hz, $^2J_{PC}$ = 12.4 Hz), 64.6 (d, *C*H$_2$CH$_3$, $^2J_{PC}$ = 6.2 Hz), 15.5 (d, *C*H$_3$, $^3J_{PC}$ = 7.0 Hz), 5.6 (dd, C_γ, $^2J_{PC}$ = 12.8 Hz, $^2J_{PC}$ = 9.0 Hz); ^1H NMR ($CDCl_3$; 250.1 MHz; 298 K) δ 7.94–6.44 (m, Ph *H*), 3.35 (m, CH_2CH$_3$, $^3J_{HH}$ = 7.1 Hz), 1.54 (s, $C_\gamma H_2$), 0.99 (t, CH$_2$CH_3, $^3J_{HH}$ = 7.1 Hz). Anal. Calcd for $C_{33}H_{32}O_9P_2Ru_2$: C, 47.37; H, 3.85; P, 7.40. Found: C, 47.12; H, 4.00; P, 7.26.

(8) Spectroscopic data for compound **4**: IR ($CHCl_3$) ν(CO) 2056 (vs), 2020 (vs), 1989 (m), 1966 (m), 1943 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$; 81.0 MHz; 298 K) δ 179.2 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$; 50.3 MHz; 298 K) δ 208.6 (d, CO, $^2J_{PC}$ = 54.4 Hz), 208.5 (d, CO, $^2J_{PC}$ = 52.6 Hz), 198.9 (s, CO), 198.3 (d, CO, $^2J_{PC}$ = 9.7 Hz), 196.7 (d, CO, $^2J_{PC}$ = 9.2 Hz), 196.6 (s, CO), 184.2 (s, C_β), 157.5–121.7 (m, *C* Ph and *C*N), 112.9 (d, C_α, $^2J_{PC}$ = 18.9 Hz), 60.1 (s, *t*-Bu *C*), 28.8 (s, *t*-Bu *C*H$_3$); 5.0 (d, C_γ, $^2J_{PC}$ = 8.5 Hz); ^1H NMR ($CDCl_3$; 200.1 MHz; 298 K) δ 7.83–7.04 (m, Ph *H*), 1.54 (s, $C_\gamma H_2$), 0.99 (s, t-Bu CH_3). Anal. Calcd for $C_{32}H_{26}NO_6PRu_2{\cdot}0.33C_7H_8$: C, 52.57; H, 3.68. Found: C, 52.82; H, 3.98.

(9) Spectroscopic data for compound **5**: IR ($CHCl_3$) ν(CO) 2049 (vs), 2011 (vs), 1979 (s), 1956 (m), 1931 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2; 81.0 MHz; 298 K) δ 182.5 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2; 50.3 MHz; 298 K) δ 211.2 (d, CO, $^2J_{PC}$ = 54.0 Hz), 211.0 (d, CO, $^2J_{PC}$ = 57.0 Hz), 200.3 (s, CO), 198.6 (d, CO, $^2J_{PC}$ = 9.1 Hz), 198.2 (s, CO), 197.9 (d, CO, $^2J_{PC}$ = 8.7 Hz), 169.3 (s, N–*C*–N), 164.5 (d, C_α, $^2J_{PC}$ = 10.0 Hz), 155.8 (s, C_β), 146.0–124.2 (m, Ph *C*), 52.8 (s, *t*-Bu *C*), 40.9 (s, *C*H$_2$CH$_3$), 28.6 (s, *t*-Bu *C*H$_3$), 15.1 (s, CH$_2$*C*H$_3$), 8.8 (d, C_γ, $^2J_{PC}$ = 8.7 Hz); ^1H NMR (CD_2Cl_2; 200.1 MHz; 298 K) δ 8.02–6.85 (m, Ph *H*), 4.74 (br s, *H*NEt), 3.54 (br s, HN-*t*-Bu), 3.32 (ddq, N–CH_2, $^3J_{HCH_3}$ = 7.2 Hz, $^3J_{HNH}$ = 7.2 Hz, $^2J_{HH}$ = 12.6 Hz), 3.10 (ddq, N–CH_2, $^3J_{HCH_3}$ = 7.2 Hz, $^3J_{HNH}$ = 7.2 Hz, $^2J_{HH}$ = 12.6 Hz), 1.33 (dd, $C_\gamma H_2$, $^3J_{PH}$ = 4.6 Hz, $^2J_{HH}$ = 16.5 Hz), 1.09 (t, N–CH$_2$–CH_3, $^3J_{HH}$ = 7.2 Hz), 0.96 (dd, $C_\gamma H_2$, $^3J_{PH}$ = 5.0 Hz, $^2J_{HH}$ = 16.5 Hz), 0.81 (s, *t*-Bu CH_3). Anal. Calcd for $C_{34}H_{33}N_2O_6PRu_2$: C, 51.13; H, 4.16; N, 3.51. Found: C, 51.06; H, 4.05; N, 3.44.

(10) Spectroscopic data for complex **6**: IR ($CHCl_3$) ν(CO) 2051 (vs), 2013 (vs), 1980 (s), 1959 (m), 1935 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2; 81.0 MHz; 298 K) δ 182.5 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2; 50.3 MHz; 298 K) δ 211.3 (d, CO, $^2J_{PC}$ = 53.6 Hz), 210.7 (d, CO, $^2J_{PC}$ = 57.8 Hz), 199.8 (s, CO), 199.6 (s, C_β), 198.4 (d, CO, $^2J_{PC}$ = 9.4 Hz), 197.8 (s, CO), 197.7 (d, CO, $^2J_{PC}$ = 9.2 Hz), 155.3 (s, N–*C*–S), 145.8–124.5 (m, Ph *C*), 125.6 (s, C_α), 58.7 (s, *t*-Bu *C*), 31.8 (s, *C*H$_2$CH$_3$), 27.4 (s, *t*-Bu *C*H$_3$), 13.6 (s, CH$_2$*C*H$_3$), 11.3 (d, $C_\gamma H_2$, $^2J_{PC}$ = 8.9 Hz); ^1H NMR (CD_2Cl_2; 200.1 MHz; 298 K) δ 8.27–6.94 (m, Ph *H*), 5.38 (br s, *H*N-*t*-Bu), 3.17 (m, CH_2CH$_3$), 3.00 (m, CH_2CH$_3$), 1.37 (m, $C_\gamma H_2$), 1.32 (t, CH$_2$CH_3, $^3J_{HH}$ = 7.5 Hz), 0.93 (s, *t*-Bu CH_3). Anal. Calcd for $C_{34}H_{32}NO_6PRu_2S{\cdot}0.5CH_2Cl_2$: C, 48.28; H, 3.86; N, 1.63; P, 3.61; S, 3.74. Found: C, 48.87; H, 4.10; N, 1.69; P, 3.66; S, 3.73.

(11) Crystal data for **2a**: $C_{29}H_{24}NO_6PRu_2$, M_r = 715.6; monoclinic, space group $P2_1/n$, a = 16.554 (4) Å, b = 20.372 (4) Å, c = 17.881 (4) Å, β = 107.50 (2)°, V = 5751 (2) Å^3, Z = 8, T = 200 K, D_c = 1.653 g cm^{-3}, $F(000)$ = 2848, λ = 0.710 73 Å, μ(Mo Kα) = 11.1 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.30 × 0.34 × 0.39 mm mounted on a Nicolet-Siemens R3m/V diffractometer by the 2θ–θ-scan method ($2\theta < 50°$). From 10 168 measured data 7137 with $F > 6\sigma(F)$ were observed and used in the structure solution (Patterson, Fourier methods) and refinement (full-matrix least squares) to R and R_w values of 0.058 and 0.095, respectively. The data crystal was twinned, with the minor twin component estimated at only 6% of the host crystal and related to it by a translation of 0x, 0.16y, 0.5z. The ruthenium and phosphorus atoms of the twin were resolvable and were included in the refinement with occupancies of 0.06. All non-hydrogen atoms were refined anisotropically. No attempt was made to include H atoms in the refinement. Crystal data for **3a**: $C_{39}H_{40}O_6P_2Ru_2$, M_r = 868.8, monoclinic, space group $P2_1/n$, a = 11.174 (2) Å, b = 20.272 (3) Å, c = 16.941 (3) Å, β = 91.94 (1)°, V = 3835 (1) Å^3, Z = 4, T = 294 K, D_c = 1.505 g cm^{-3}, $F(000)$ = 1760, λ = 0.710 73 Å, μ(Mo Kα) = 8.97 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.27 (010) × 0.32 (001) × 0.33 (101) × 0.48 (101) mm mounted on a Nicolet-Siemens R3m/V diffractometer by the ω-scan method ($2\theta < 50°$). The structure solution and refinement were based on 5130 observed data (6753 measured). Final R and R_w values were 0.027 and 0.033, respectively. All non-hydrogen atoms were refined anisotropically, and all hydrogens were refined with isotropic thermal coefficients. Crystal data for **5**: $C_{34}H_{33}N_2O_6PRu_2{\cdot}CH_2Cl_2$, M_r = 883.7, triclinic, space group $P1$, a = 11.389 (3) Å, b = 11.549 (2) Å, c = 15.650 (4) Å, α = 79.76 (2)°, β = 69.42 (2)°, γ = 83.39 (2)°, V = 1893.2 (7) Å, Z = 2, T = 200 K, D_c = 1.551 g cm^{-3}, $F(000)$ = 888, λ = 0.710 73 Å, μ(Mo Kα) = 10.09 cm^{-1}. Intensity data were collected on a prism of dimensions 0.40 × 0.40 × 0.49 mm, as described for **3a**. The structure was refined to R = 0.029 and R_w = 0.042 on the basis of 5902 observed (6695 measured) reflections. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically.

(12) EHMO calculations were carried out with use of a version of the ICON-8 program (Program ICON 8: Howell, J.; Rossi, A.; Wallace, D.; Haraki, K.; Hoffmann, R. *QCPE 517* **1986**, *6*, 100) modified by Dr. D. A. Pensak of the Du Pont Central Research and Development Laboratory (Pensak, D. A.; McKinney, R. J. *Inorg. Chem.* **1979**, *18*, 3407 and references therein). We are grateful to Dr. A. Cherkas for advice on these calculations.

C_β becomes dominant and maximizes at rotation of the $C_\gamma H_2$ unit of 88° with respect to the CH_2 plane in the ground state. Concomitantly, a positive charge develops on C_β, while C_α and C_γ still bear negative charges. Thus, nucleophilic attack at C_β appears to be favored by both charge and orbital factors.

These preliminary results suggest a rich chemistry for μ-η^1:η^2-allenyl complexes as a source of three-carbon fragments in synthesis.

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Supplementary Material Available: Tables of structure determination details, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for **2a**, **3a**, and **5** (26 pages); tables of observed and calculated structure factors (86 pages). Ordering information is given on any current masthead page.

Models for Organometallic Molecule–Support Complexes. Very Large Counterion Modulation of Cationic Actinide Alkyl Reactivity

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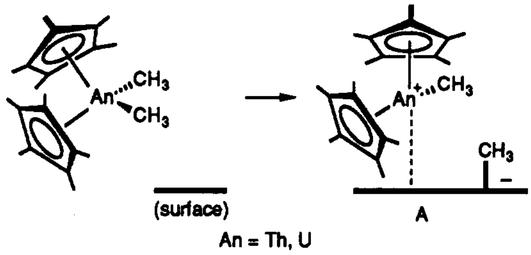
Summary: The reaction of $Cp'_2Th(CH_3)_2$ ($Cp' = \eta^5$-$(CH_3)_5C_5$) with $HN^nBu_3{}^+B(C_6F_5)_4{}^-$ yields the crystallographically characterized, cationic thorium alkyl $Cp'_2ThCH_3{}^+B(C_6F_5)_4{}^-$. The $B(C_6F_5)_4{}^-$ anion is weakly coordinated, the NMR spectroscopic parameters are similar to those of $Cp'_2Th(CH_3)_2$ adsorbed on dehydroxylated alumina, and the complex is a highly active catalyst for ethylene polymerization and 1-hexene hydrogenation.

Surface spectroscopic[1] and chemical[2] evidence argue that cationic alkyls play a major role in facile olefin transformations catalyzed by organoactinides adsorbed on electron-deficient supports (e.g., A in eq 1). Furthermore, analogous group 4 species[3,4] are thought to be important in homogeneous Ziegler–Natta catalysis.[5] Nevertheless, an *isolable, structurally characterized, base-free* complex that models both the salient spectroscopic and catalytic properties of A has not been available. We report here on



(1)

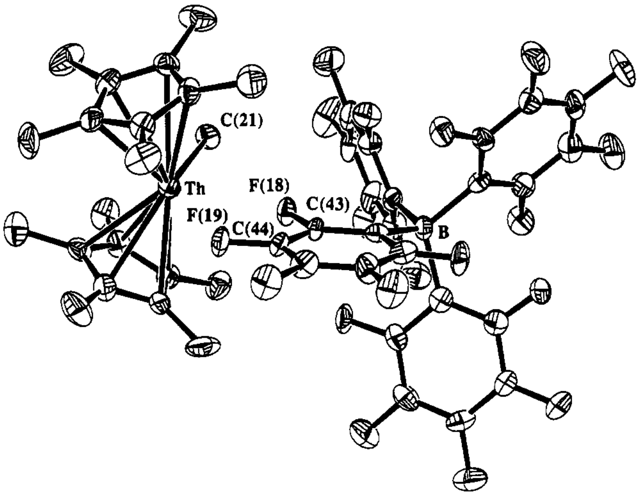


Figure 1. Molecular structure of $Cp'_2ThCH_3{}^+B(C_6F_5)_4{}^-$ (1). Important bond distances (Å) and angles (deg) are as follows: Th–C(21) = 2.399 (8), Th–C_{ring} = 2.754 (3) (av), Th–F(18) = 2.757 (4), Th–F(19) = 2.675 (5), C(43)–F(18) = 1.325 (6), C(44)–F(19) = 1.344 (7); ring centroid–Th–ring centroid = 140.1 (3). Thermal ellipsoids are drawn at the 35% probability level.

Table I. Solution-Phase Catalytic Activity of $Cp_2'ThCH_3{}^+X^-$ Complexes[a]

	X^-			
reaction	CH_3^-	$^1/_2$ Fe(1,2-$C_2B_9H_{11})_2{}^{2-}$	BPh_4^-	$B(C_6F_5)_4^-$
ethylene polymerization[b]	0	0	1.1×10^{-2}	36
1-hexene hydrogenation[c]	1.4×10^{-4}	0	1.1×10^{-3}	4.57

[a] As expressed in turnover frequencies (N_t, s^{-1}). [b] Procedure of ref 15: $P_{ethylene}$ = 1.0 atm, T = 25 °C, solvent toluene or benzene. [c] Procedure of ref 15: P_{H_2} = 1.0 atm, T = 25 °C, solvent toluene or benzene.

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