Reactions of Iminophosphorano(8-quinolyl)methane with $AlMe_3$: Unexpected Formation of Aluminum Iminophosphorano(2-methyl-8-quinolyl)methandiide Complex

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Reaction of $Ph_2P(8\text{-}CH_2C_9H_6N)=NBu^t$ (**1**) with 2 equiv of $AlMe_3$ in toluene under reflux conditions afforded aluminum iminophosphorano(2-methyl-8-quinolyl)methandiide complex (**2**). The reaction proceeded via the intermediates of a coordination complex, $[(AlMe_3)\{Ph_2P(8\text{-}CH_2C_9H_6N)=NBu^t\}]$ (**3**), and then an addition complex (**4**) of $AlMe_3$ to the carbon−nitrogen double bond of the quinolyl ring of the neutral ligand. The coordination complex was converted to the singly deprotonated complex $[(AlMe_2)\{CH(8\text{-}C_9H_6N)(Ph_2P=NBu^t)\}]$ (**5**) at 60 °C, which further reacted with $AlMe_3$ in toluene under reflux conditions to yield aluminum iminophosphorano(8-quinolyl)methandiide (**6**). The structures of complexes **2**, **4**, and **6** were proved by single-crystal X-ray diffraction techniques, and the five-coordinate complexes **3** and **5** were characterized by ^{27}Al NMR spectroscopy.

Introduction

Organoaluminum compounds with nitrogen-containing ligands have attracted much attention in recent years due to their use as precursors to nitride materials and as catalysts.[1] These compounds also show versatile coordination modes and reactivities.[2] For example, the low-coordinate cationic aluminum compounds have demonstrated enhanced activities in olefin polymerization.[3] For ligands, monofunctional amides, phosphinimides, chelating *N*,*N*-amidinates, guanidinates, and diketiminates are most prevalent.[4] We report here a new functionalized iminophosphorane ligand, $Ph_2P(8\text{-}CH_2C_9H_6N)=NBu^t$ (C_9H_6N = quinolyl), and its reactions with $AlMe_3$. The reactions formed coordination complexes, both singly and doubly deprotonated complexes of the methylene of the ligand and the rare addition complex of $AlMe_3$ to the carbon−nitrogen double bond of the quinolyl ring.

Results and Discussion

The neutral ligand **1** was prepared by deprotonation of the phosphonium salt $[Ph_2(Bu^tNH)(8\text{-}CH_2C_9H_6N)P]^+Br^-$ (prepared by reaction of Bu^tNHPPh_2[5] with 8-bromomethylquinoline[6]) using NaH in THF. Treatment of **1** with 2 equiv of $AlMe_3$ in toluene at 120 °C afforded the bimetallic aluminum iminophosphorano(2-methyl-8-quinolyl)methandiide complex (**2**) in 49% yield (Scheme 1). The reaction intermediate **4** was obtained in good yield by action of **1** with over 1 equiv of $AlMe_3$ at room temperature or 60 °C. Reaction of **4** with 1 equiv of $AlMe_3$ at 120 °C produced **2** via elimination of $HAlMe_2$ and methane as well as further elimination of H_2. However, no reaction occurred when heating **4** in the absence of $AlMe_3$. This showed that the elimination of methane in the reaction of $AlMe_3$ with **4** may be prior. Apparently **4** is an addition product of $AlMe_3$ to the carbon−nitrogen double bond of the quinolyl ring of **1**. Usually addition of trialkylaluminum to a carbon−nitrogen double bond of a nitrogen-containing heterocyclic compound is difficult, although the additions of $AlMe_3$ to the carbon−nitrogen double bond of a Schiff base are known.[3b,7] In a control experiment we found that the reaction between quinoline and 2 equiv of $AlMe_3$ in toluene under reflux conditions for 5 h yielded only the coordination complex $[AlMe_3{\cdot}C_9H_7N]$ in high

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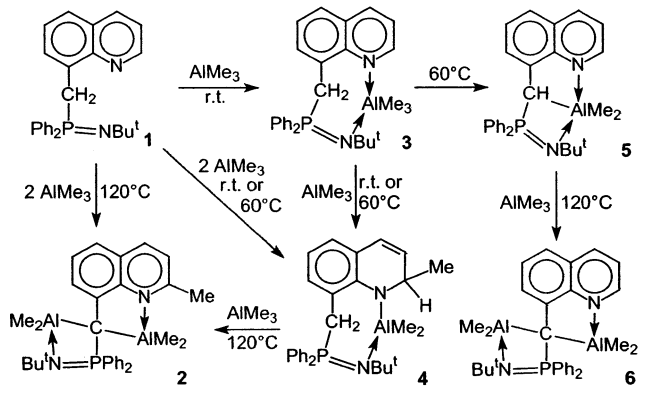
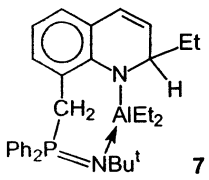
Scheme 1



yield. Hence it seems that an additional donor group, an iminophosphorano group, promotes the addition reaction of $AlMe_3$ to **1**. It was also observed that more than 1 equiv of $AlMe_3$ was necessary to carry out the addition reaction. Action of an equimolar amount of $AlMe_3$ with **1** at room temperature formed a coordination complex, presumably **3** (Scheme 1), which further reacted with $AlMe_3$ to give complex **4** in 96% yield. In fact, the addition reaction of **3** with $AlMe_3$ can be completed in the presence of a catalytic amount of $AlMe_3$. The extra $AlMe_3$ could act as an external alkylating agent. The reaction of the coordination complex **3** with $AlMe_3$ formed an equivalent of $AlMe_3$ besides the addition complex **4**, and the released $AlMe_3$ may continue the addition reaction to the unreacted **3**. This was also proved by reaction of complex **3** with $AlEt_3$. Action of **3** with 1 equiv of $AlEt_3$ gave a brownish-yellow oil. The ^1H NMR spectrum showed that it was a mixture of **4** and **7** with impurities, while the reaction of **3** with a catalytic amount of $AlEt_3$ afforded complex **4**. The above reaction provides a route of alkylation of



the quinoline ring. Some other metal-mediated alkylations of quinoline and pyridine are also known.[8−12] In the absence of $AlMe_3$ **3** was almost quantitatively converted to **5** at 60 °C in 2 h either in a sealed NMR tube in C_6D_6 or in a preparative scale in benzene or toluene. Further reaction of **5** with 1 equiv of $AlMe_3$ in toluene under reflux conditions afforded another bimetallic aluminum methandiide complex, **6**, in 92% yield via elimination of methane. A structurally related

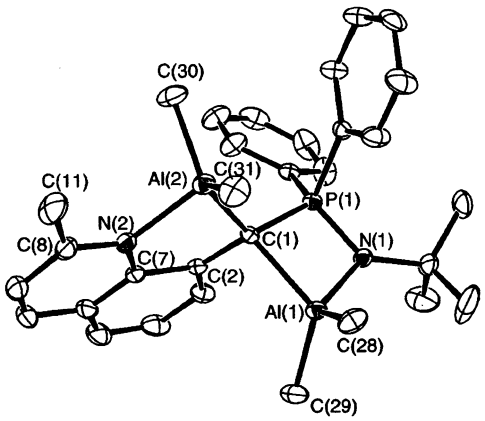


Figure 1. ORTEP diagram of complex **2** with 20% probability thermal ellipsoids. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Al(1)−C(1) 2.126(4), Al(2)−C(1) 2.014(4), Al(1)−N(1) 1.920(3), Al(2)−N(2) 1.999(4), P(1)−C(1) 1.745(4), P(1)−N(1) 1.611(3); C(1)−Al(1)−N(1) 78.87(13), C(1)−Al(2)−N(2) 85.54(15), Al(1)−C(1)−Al(2) 121.20(16), C(1)−P(1)−N(1) 100.14.

bimetallic methandiide complex of aluminum, $[(AlMe_2)_2\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C',N,N'\}]$, has been reported.[13] Other dialuminiomethane derivatives are also known.[14]

Compounds **1**−**6** have been characterized by elemental analysis and ^1H, ^{13}C, ^{31}P, and ^{27}Al (for **3** and **5**) NMR spectroscopy. To assist the assignments of the signals of the ^1H NMR spectrum of **4**, a 2D H−H COSY NMR spectrum was also run. The ^{13}C signals of the quaternary methanediide carbon in **2** and **6** were not observed. The ^1H NMR spectrum of complex **4** showed that the two protons of the methylene have different chemical environments, the chemical shifts appearing at 2.51 and 4.66 ppm, respectively. The upfield signal may be due to agostic interaction between the proton and the aluminum atom. The ^{27}Al NMR spectra of complexes **3** and **5** show resonances at 70.57 and 69.38 ppm, respectively, consistent with the existence of five-coordinate aluminum centers.[15]

Complexes **2**, **4**, and **6** were further characterized by X-ray crystallography. The molecular structure of complex **2** is showed in Figure 1 along with selective bond lengths and angles. The complex has a spirocyclic skeleton that comprises a five-membered metallacyclic ring and a four-membered metallacyclic ring fused at C(1). The spiro carbon atom is distorted tetrahedral with angles ranging from 84.67(16)° to 121.20(16)°. Each aluminum atom has a distorted tetrahedral geometry. The C(1)−Al(2)−N(2) bond angle [85.54(15)°] is wider than that of C(1)−Al(1)−N(1) [78.87(13)°] due to difference of the ring sizes, and the latter is close to those

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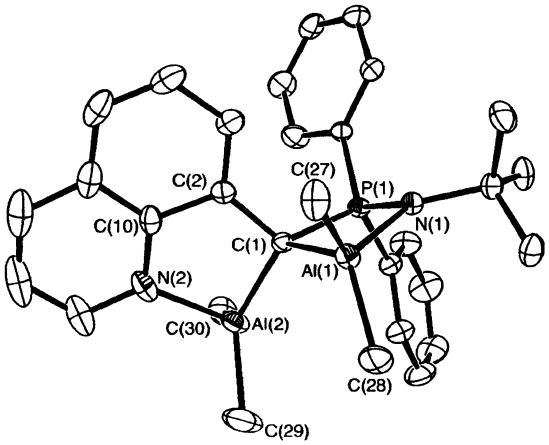

Figure 2. ORTEP diagram of complex **6** with 20% probability thermal ellipsoids. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Al(1)−N(1) 1.925(3), Al(1)−C(1) 2.132(4), Al(2)−N(2) 1.985(4), Al(2)−C(1) 2.006(4), P(1)−N(1) 1.620(3), P(1)−C(1) 1.754(4), C(1)−C(2) 1.495(5); N(1)−Al(1)−C(1) 79.30(13), N(2)−Al(2)−C(1) 85.94(16), Al(2)−C(1)−Al(1) 121.69(17), N(1)−P(1)−C(1) 100.42(16), P(1)−N(1)−Al(1) 95.06(14).

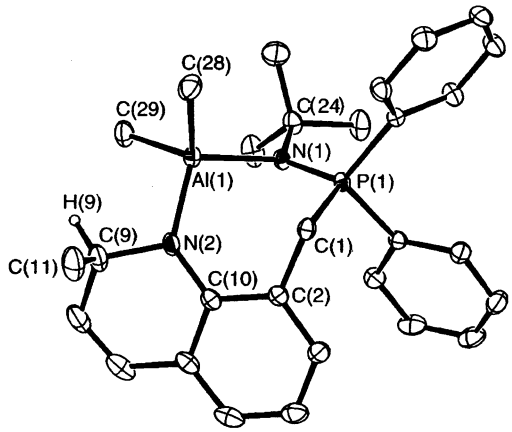

Figure 3. ORTEP diagram of complex **4** with 20% probability thermal ellipsoids. All hydrogen atoms except that on C(9) have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Al(1)−N(1) 1.988(2), Al(1)−N(2) 1.892(2), P(1)−C(1) 1.810(2), P(1)−N(1) 1.614(2), C(9)−N(2) 1.491(3), C(10)−N(2) 1.378(3); N(1)−Al(1)−N(2) 107.33(9), N(1)−Al(1)−C(28) 107.97(11), C(28)−Al(1)−C(29) 106.98(14), C(1)−P(1)−N(1) 107.50(11), P(1)−N(1)−Al(1) 116.60(11), C(10)−N(2)−Al(1) 130.70(17), N(2)−C(9)−C(8) 112.1(3).

found in $[(AlMe_2)_2\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C'N,N'\}]$ (av 80.0°).[13] The Al(1)−C(1) distance of 2.216(4) Å is longer than that of Al(2)−C(1), 2.014(4) Å, and both are comparable to corresponding distances in $[(AlMe_2)_2\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C'N,N'\}]$, 2.117(3) and 2.121(3) Å, respectively.[13] The Al(2)−N(2) distance of 1.999(4) Å is longer than that of Al(1)−N(1), 1.920(3) Å, and is also longer than those in $[(AlMe_2)_2\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C'N,N'\}]$ (av 1.930 Å), but still within the usual range.[2d,4a,c,16]

The monomeric crystalline complex **6** has a skeletal structure very similar to **2** (Figure 2), and the bond lengths and bond angles are also comparable to corresponding ones in complex **2**.

The molecular structure of complex **4** is shown in Figure 3 along with selective bond lengths and angles. The complex is a monomer in which the two nitrogen atoms of the ligand chelate to an aluminum center to form a seven-membered metallacyclic ring with Al(1), N(1), P(1), C(1), C(2), C(10), and N(2) atoms adopting a distorted boat conformation. The coordination geometry at aluminum is distorted tetrahedral with angles ranging from 105.60(12)° to 115.34(12)°. The distance of the aluminum atom to the iminophosphorano-nitrogen atom [1.988(2) Å] is significantly longer than that to the formally negatively charged nitrogen atom [1.892(2) Å]. The bond angles at C(9) ranging from 110.1(3)° to 112.1(3)° reflect an sp^3 hybrid of C(9). The sum of the bond angles at N(2) is 359.48°, indicating that the atoms N(2), Al(1), C(9), and C(10) lie in a plane.

Summary

We have described the reactions of an iminophosphorane-methylene-quinoline compound, $Ph_2P(8\text{-}CH_2C_9H_6N){=}NBu^t$, with $AlMe_3$. The products formed are dependent on the reaction conditions and the ratio of the reactants. Reaction of $Ph_2P(8\text{-}CH_2C_9H_6N){=}NBu^t$ with 2 equiv of $AlMe_3$ in toluene under reflux conditions afforded spirocyclic aluminum iminophosphorano(2-methyl-8-quinolyl)-methandiide (**2**), while stepwise reaction of $Ph_2P(8\text{-}CH_2\text{-}C_9H_6N){=}NBu^t$ with $AlMe_3$ gave spirocyclic aluminum iminophosphorano(8-quinolyl)methandiide (**6**). Complex **2** was formed via the intermediates of a coordination complex of $AlMe_3$ with the neutral ligand and an addition complex (**4**) of $AlMe_3$ to the carbon−nitrogen double bond of the quinolyl ring of $Ph_2P(8\text{-}CH_2C_9H_6N){=}NBu^t$, while complex **6** was yielded via the coordination complex and then a singly deprotonated complex of the ligand, $[AlMe_2\{CH(8\text{-}C_9H_6N)(Ph_2P{=}NBu^t)\}]$. Complex **4** also provides a rare example of addition of trialkylaluminum to a carbon−nitrogen double bond of a nitrogen-containing heterocyclic compound.

Experimental Section

Gerneral Procedures. All experiments were performed under nitrogen using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium-benzophenone (benzene, THF, Et_2O, and *n*-hexane), or CaH_2 (CH_2Cl_2) and degassed prior to use. $CDCl_3$ and C_6D_6 were purchased from Acros Organics and degassed and stored over activated molecular sieves ($CDCl_3$) or Na/K alloy (C_6D_6). $LiBu^n$ and Ph_2PCl were purchased from Acros Organics and used as obtained. $AlMe_3$ and $AlEt_3$ was purchased from Alfa Aesar and used as received. Bu^tNHPPh_2[5] and 8-bromomethylquinoline[6] were prepared according to literature. NMR spectra were recorded on a Bruker av400 or av300 spectrometer at ambient temperature. The chemical shifts of ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to internal solvent resonances, the $^{31}P\{^1H\}$ NMR spectra are referenced to external 85% H_3PO_4, and the ^{27}Al NMR spectra are referenced to external $AlCl_3$. Infrared spectra were recorded on a Bruker VECTOR-22 spectrometer. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry and the Analytical Center of the University of Science and Technology of China.

Preparation of $[Ph_2(8\text{-}CH_2quinolyl)(NHBu^t)P]^+Br^-$. To a solution of 8-bromomethylquinoline (7.22 g, 32.81 mmol) in

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80 mL of CH_2Cl_2 was added Ph_2PNHBu^t (8.40 g, 32.64 mmol) at room temperature with stirring. The mixture was stirred for 8 h and then the solvent removed under vacuum. Benzene was added to the viscous residue to form a white crystalline solid (13.45 g, 86%), mp 230−233 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.17 (s, 9H, Bu^t), 5.29 (d, J = 16.0 Hz, 2H, CH_2), 7.20−7.43 (m, 5H, Ar), 7.56 (t, J = 6.8 Hz, 2H, Ar), 7.72 (dd, J = 7.7, 12.6 Hz, 5H, Ar), 7.99 (s, 1H, Ar), 8.12 (s, 1H, Ar), 8.47 (d, J = 3.5 Hz, 1H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 30.68 (d, J = 64.7 Hz, CH_2), 32.09 (d, J = 4.3 Hz, Bu^t), 55.70 (d, J = 5.5 Hz, Bu^t), 121.63, 121.74, 123.01, 127.10, 127.66, 128.46 (d, J = 2.6 Hz), 128.78 (d, J = 4.1 Hz), 129.36 (d, J = 12.8 Hz), 133.76 (d, J = 10.4 Hz), 134.63 (d, J = 2.9 Hz), 138.01, 145.77, 149.11. ^{31}P{^{1}H} NMR ($CDCl_3$): δ (ppm) 37.35.

Preparation of $Ph_2P(8\text{-}CH_2quinolyl)$═$NBu^t$ (1). A mixture of $[Ph_2(8\text{-}CH_2quinolyl)(NHBu^t)P]^+Br^-$ (1.55 g, 3.24 mmol) and NaH (0.16 g, 6.67 mmol) in THF (20 mL) was stirred overnight at room temperature and then refluxed for 2 h. The mixture was filtered, and the solvent was removed from the filtrate under vacuum. The residue was recrystallized in hexane to give colorless crystalline **1** (1.08 g, 84%), mp 114−116 °C. ^{1}H NMR (C_6D_6): δ (ppm) 1.47 (s, 9H, Bu^t), 4.80 (d, J = 13.7 Hz, 2H, CH_2), 6.71 (dd, J = 4.1, 8.2 Hz, 1H, Ar), 6.94−6.96 (m, 6H, Ar), 7.12−7.17 (m, 2H, Ar), 7.43 (dd, J = 1.5, 8.2 Hz, 1H, Ar), 7.77−7.84 (m, 4H, Ar), 8.11 (d, J = 6.7 Hz, 1H, Ar), 8.61−8.63 (m, 1H, Ar). ^{13}C{^{1}H} NMR (C_6D_6): δ (ppm) 32.26 (d, J = 61.1 Hz, CH_2), 36.17 (d, J = 10.6 Hz, Bu^t), 52.42 (Bu^t), 120.94, 126.55 (dd, J = 2.7, 9.7 Hz), 128.26, 130.49 (d, J = 2.6 Hz), 131.35 (d, J = 5.2 Hz), 132.73 (d, J = 9.1 Hz), 134.12 (d, J = 6.8 Hz), 136.30, 136.68, 137.94, 147.81 (d, J = 5.4 Hz), 149.24. ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 18.99. IR (KBr): ν (cm^{-1}) 1269$_{vs}$ (P═N). Anal. Calcd for $C_{26}H_{27}N_2P$: C, 78.37; H, 6.83; N, 7.03. Found: C, 77.97; H, 6.82; N, 6.89.

Preparation of $[(AlMe_2)_2\{C(Ph_2P$═$NBu^t)(2\text{-}Me\text{-}8\text{-}quinolyl)\}]$ (2). (1) By Reaction of Compound 1 with 2 Equiv of $AlMe_3$ in Toluene at 120 °C. To a solution of **1** (0.34 g, 0.85 mmol) in toluene (15 mL) was added $AlMe_3$ (2.3 M solution in hexane, 0.74 mL, 1.70 mmol) at room temperature with stirring. The mixture was stirred at room temperature overnight and at 120 °C (bath temperature) for 5 h. The solvent was removed under vacuum. The residue was dissolved in Et_2O and then filtered. Concentration of the filtrate afforded yellow crystals of **2** (0.22 g, 49%), mp 256 °C (dec). ^{1}H NMR (C_6D_6): δ (ppm) −1.01 (s, 3H, Al-Me), −0.51 (s, 3H, Al-Me), 0.21 (s, 3H, Al-Me), 0.30 (s, 3H, Al-Me), 1.33 (s, 9H, Bu^t), 2.29 (s, 3H, Ar-Me), 6.16 (d, J = 8.3 Hz, 1H, Ar), 6.70 (d, J = 7.9 Hz, 1H, Ar), 6.89−6.95 (m, 4H, Ar), 7.06−7.14 (m, 5H, Ar), 7.85−7.91 (m, 2H, Ar), 8.03−8.10 (m, 2H, Ar). ^{13}C{^{1}H} NMR (C_6D_6): δ (ppm) −7.14 (Al-Me), −5.94 (Al-Me), −4.23 (Al-Me), −1.72 (Al-Me), 22.97 (Me), 34.00 (d, J = 7.5 Hz, Bu^t), 52.85 (d, J = 8.6 Hz, Bu^t), 118.03, 123.45, 126.91, 127.29, 128.98, 129.13, 130.39, 130.79, 131.12 (d, J = 10.7 Hz), 131.34, 131.71 (d, J = 9.6 Hz), 134.05 (d, J = 9.5 Hz), 137.79, 138.93, 140.66, 145.73 (d, J = 17.7 Hz), 146.46. ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 36.53. Anal. Calcd for $C_{31}H_{39}N_2PAl_2$: C,70.98; H, 7.49; N, 5.34. Found: C, 71.36; H, 7.82; N, 5.59.

(2) By Reaction of Complex 4 with 1 Equiv of $AlMe_3$ in Toluene at 120 °C. To a solution of **4** (0.30 g, 0.64 mmol) in toluene (10 mL) was added $AlMe_3$ (2.3 M solution in hexane, 0.28 mL, 0.64 mmol) at room temperature. The mixture was stirred at room temperature for 2 h and at 120 °C (bath temperature) for 5 h. The solvent was removed under vacuum. The residue was dissolved in Et_2O and then filtered. Concentration of the filtrate produced yellow crystals identified as **2** (0.17 g, 51%).

Preparation of $[AlMe_3\{Ph_2P(8\text{-}CH_2quinolyl)$═$NBu^t\}]$ (3). To a benzene (10 mL) solution of compound **1** (0.34 g, 0.85 mmol) was added $AlMe_3$ (2.3 M solution in hexane, 0.36 mL, 0.83 mmol) with stirring at room temperature. A white precipitate was formed after a few minutes. The stirring was continued for 3 h. The precipitate was filtered, washed with benzene, and dried under vacuum to give a white powder of **3** (0.33 g, 82%), mp 119−121 °C. ^{1}H NMR (C_6D_6): δ (ppm) 0.39 (s, 9H, Al-Me), 1.49 (s, 9H, Bu^t), 5.48 (d, J = 18.4 Hz, 2H, CH_2), 6.54 (dd, J = 4.1, 8.1 Hz, 1H, Ar), 6.72−6.84 (m, 4H, Ar), 6.92−7.00 (m, 3H, Ar), 7.15−7.20 (m, 2H, Ar), 7.56−7.63 (m, 3H, Ar), 7.80−7.86 (m, 2H, Ar), 8.10−8.15 (m, 1H, Ar). ^{13}C{^{1}H} NMR (C_6D_6): δ (ppm) 0.84 (Al-Me), 33.35 (Bu^t), 33.74 (d, J = 65.8 Hz, CH_2), 52.50 (Bu^t), 120.66, 122.79, 125.58, 126.17, 128.67, 129.33, 131.06, 131.46, 132.43, 133.16 (d, J = 9.8 Hz), 133.65 (d, J = 8.1 Hz), 134.08 (d, J = 9.6 Hz), 135.12, 139.39, 147.47, 148.46, 149.31. ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 33.21. ^{27}Al NMR (C_6D_6): δ (ppm) 70.57 ($w_{1/2}$ = 3600 Hz). Anal. Calcd for $C_{29}H_{36}N_2PAl$: C, 74.02; H, 7.71; N, 5.95. Found: C, 73.82; H, 7.83; N, 5.89.

Preparation of Complex 4. (1) By Reaction of $Ph_2P(8\text{-}CH_2quinolyl)$═$NBu^t$ with 2 Equiv of $AlMe_3$. To a solution of **1** (0.57 g, 1.43 mmol) in toluene (10 mL) was added $AlMe_3$ (2.3 M solution in hexane, 1.24 mL, 2.85 mmol) at room temperature. The mixture was stirred at room temperature overnight and at 60 °C for 4 h. The mixture was filtered, and the filtrate was concentrated under vacuum to afford pale yellow crystals of **4** (0.50 g, 75%), mp 190 °C (dec). ^{1}H NMR (C_6D_6): δ (ppm) 0.00 (s, 3H, Al-Me), 0.22 (s, 3H, Al-Me), 1.19 (s, 9H, Bu^t), 1.25 (d, J = 6.5 Hz, 3H, Me), 2.51 (dd, J = 14.7, 7.6 Hz, 1H, P-CH), 4.56 (quintet, J = 6.2 Hz, 1H, NCH), 4.66 (dd, J = 14.7, 16.7 Hz, 1H, P-CH), 5.88 (dt, J = 2.1, 7.4 Hz, 1H, Ar), 5.97 (dd, J = 5.9, 9.2 Hz, 1H, CH═CH), 6.34 (td, J = 0.8, 7.4 Hz, 1H, Ar), 6.50 (d, J = 9.3 Hz, 1H, CH═CH), 6.86−6.96 (m, 2H, Ar), 6.98−7.02 (m, 2H, Ar), 7.06−7.09 (m, 3H, Ar), 7.25−7.31 (m, 2H, Ar), 7.72−7.77 (m, 2H, Ar). ^{13}C{^{1}H} NMR (C_6D_6): δ (ppm) −1.90 (Al-Me), 0.75 (Al-Me), 22.57 (Me), 33.79 (d, J = 7.40 Hz, Bu^t), 37.54 (d, J = 71.5 Hz, CH_2), 48.83 (NCH), 57.06 (d, J = 7.1 Hz, Bu^t), 113.59, 116.94 (d, J = 10.2 Hz), 125.10, 126.05, 126.78, 128.74, 128.89, 129.11, 130.09, 130.69 (d, J = 4.9 Hz), 131.16, 132.17, 132.38, 133.18 (d, J = 9.1 Hz), 133.65 (d, J = 8.7 Hz), 150.95. ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 33.27. Anal. Calcd for $C_{29}H_{36}N_2PAl$: C,74.02; H 7.71; N, 5.95. Found: C,74.19; H, 7.99; N, 5.49.

(2) By Reaction of $Ph_2P(8\text{-}CH_2quinolyl)$═$NBu^t$ with 1.2 Equiv of $AlMe_3$. The same method as in (1) was used, but the molar ratio of $Ph_2P(8\text{-}CH_2quinolyl)$═$NBu^t$ to $AlMe_3$ was changed to 1:1.2. After similar workup, complex **4** was obtained in 74% yield.

(3) By Reaction of $[AlMe_3\{Ph_2P(8\text{-}CH_2quinolyl)$═$NBu^t\}]$ (3) with $AlMe_3$. To a suspension of complex **3** (0.23 g, 0.49 mmol) in toluene (10 mL) was added $AlMe_3$ (2.3 M solution in hexane, 0.20 mL, 0.46 mmol) at room temperature. The mixture was stirred at room temperature overnight and at 60 °C for 2 h. The mixture was filtered, and the filtrate was concentrated under vacuum to give crystalline **4** (0.22 g, 96%).

Preparation of $[AlMe_2\{CH(8\text{-}quinolyl)(Ph_2P$═$NBu^t\}]$ (5). A suspension of complex **3** (0.27 g, 0.57 mmol) in toluene (10 mL) was stirred at 60 °C for 2 h and then filtered. The solvent was removed under vacuum to afford a pale yellow oil identified as **5** (0.25 g, 96%). ^{1}H NMR (C_6D_6): δ (ppm) 0.12 (s, 3H, Al-Me), 0.27 (s, 3H, Al-Me), 1.33 (s, 9H, Bu^t), 5.60 (d, J = 14.5 Hz, 1H, CH), 6.70−6.82 (m, 1H, Ar), 6.95−7.01 (m, 4H, Ar), 7.08−7.16 (m, 5H, Ar), 7.51−7.57 (m, 3H, Ar), 8.09−8.15 (m, 2H, Ar), 8.82 (d, J = 3.6 Hz, 1H, Ar). ^{13}C{^{1}H} NMR (C_6D_6): δ (ppm) −5.48 (Al-Me), −4.83 (Al-Me), 26.66 (d, J = 58.8 Hz, CH), 33.36 (d, J = 7.5 Hz, Bu^t), 52.54 (d, J = 5.6 Hz, Bu^t), 120.69, 122.77 (d, J = 3.9 Hz), 126.16 (d, J = 4.0 Hz), 128.54, 128.69, 129.26 (d, J = 7.5 Hz), 130.42, 131.50, 132.42 (d, J = 8.9 Hz), 133.16 (d, J = 9.8 Hz), 133.75, 134.07 (d, J = 9.7 Hz), 134.65, 136.09, 139.35 (d, J = 3.6 Hz), 147.69 (d, J = 8.7 Hz), 148.47. ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 35.02. ^{27}Al NMR (C_6D_6): δ (ppm) 69.38 ($w_{1/2}$ = 3700 Hz). Anal. Calcd for $C_{28}H_{32}N_2PAl$: C,73.99; H 7.10; N, 6.16. Found: C, 73.67; H, 7.40; N, 6.02.

Preparation of $[(AlMe_2)_2\{C(8\text{-}quinolyl)(Ph_2P$═$NBu^t)\}]$ (6). To a solution of complex **5** (0.29 g, 0.64 mmol) in toluene

Table 1. Details of the X-ray Structure Determinations of Complexes 2, 4, and 6

	2	**4**	**6**
empirical formula	$C_{31}H_{39}Al_2N_2P$	$C_{29}H_{36}AlN_2P$	$C_{30}H_{37}Al_2N_2P$
fw	524.57	470.55	510.55
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a (Å)	10.029(3)	10.912(3)	9.998(3)
b (Å)	12.015(3)	11.610(4)	22.527(6)
c (Å)	12.520(4)	13.007(4)	13.184(4)
α (deg)	89.232(5)	88.417(5)	90
β (deg)	88.610(6)	65.396(5)	95.960(5)
γ (deg)	88.114(6)	63.159(5)	90
V (Å^3)	1507.3(8)	1310.4(7)	2953.3(15)
Z	2	2	4
D_{calcd} (g/cm^3)	1.156	1.193	1.148
$F(000)$	560	504	1088
μ (mm^{-1})	0.171	0.158	0.173
θ range for data collecn (deg)	2.57 to 25.00	2.20 to 25.00	2.44 to 25.00
no. of reflns collected	7776	6810	14 659
no. of indep reflns (R_{int})	5219 ($R_{int} = 0.0473$)	4585 ($R_{int} = 0.0434$)	5177 ($R_{int} = 0.0913$)
no. of data/restraints/params	5219/0/333	4585/0/304	5177/0/323
goodness of fit on F^2	0.989	0.979	0.986
final R indices[a] [$I > 2\sigma(I)$]	$R1 = 0.0661$, $wR2 = 0.1101$	$R1 = 0.0458$, $wR2 = 0.1030$	$R1 = 0.0676$, $wR2 = 0.1152$
R indices (all data)	$R1 = 0.1462$, $wR2 = 0.1377$	$R1 = 0.0833$, $wR2 = 0.1195$	$R1 = 0.1545$, $wR2 = 0.1369$
largest diff peak and hole [e·Å^{-3}]	0.330 and −0.262	0.268 and −0.245	0.254 and −0.295

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

(10 mL) was added $AlMe_3$ (2.3 M solution in hexane, 0.28 mL, 0.64 mmol) at room temperature with stirring. The mixture was stirred at 120 °C (bath temperature) for 5 h and filtered after cooling to rt. The filtrate was concentrated under vacuum to give orange crystals (0.30 g, 92%), mp 254−256 °C. ^{1}H NMR (C_6D_6): δ (ppm) −0.97 (s, 3H, Al-Me), −0.45 (s, 3H, Al-Me), 0.29 (s, 3H, Al-Me), 0.37 (s, 3H, Al-Me), 1.41 (s, 9H, Bu^t), 6.38 (dd, J = 4.8, 8.2 Hz, 1H, Ar), 6.77 (d, J = 8.0 Hz, 1H, Ar), 7.00−7.06 (m, 4H, Ar), 7.13−7.33 (m, 5H, Ar), 7.88 (dd, J = 1.5, 4.8 Hz, 1H, Ar), 7.93−8.00 (m, 2H, Ar), 8.13−8.19 (m, 2H, Ar). ^{13}C{^{1}H} NMR (C_6D_6): δ (ppm) −6.10 (Al-Me), −5.81 (Al-Me), −2.09 (Al-Me), 33.93 (d, J = 7.7 Hz, Bu^t), 52.86 (d, J = 8.5 Hz, Bu^t), 117.71, 120.56, 127.92, 128.24, 129.25 (d, J = 12.2 Hz), 130.16 (d, J = 12.4 Hz), 130.91, 131.35, 131.48, 134.03 (d, J = 9.7 Hz), 138.08, 139.22, 140.27, 144.32, 145.66, 145.90, 147.42. ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 35.59. Anal. Calcd for $C_{30}H_{37}N_2PAl_2$: C, 70.57; H, 7.30; N, 5.49. Found: C, 70.28; H, 7.61; N, 5.32.

Crystal Structure Solution and Refinement for Complexes 2, 4, and 6. Single crystals of complexes **2**, **4**, and **6** were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Siemens CCD area-detector at 293(2) K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Semiempirical absorption corrections were applied to the data for **2** and **6**. The structures were solved by direct methods (SHELXS-97)[17] and refined against F^2 by full-matrix least-squares using SHELXL-97.[18] Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1.

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Supporting Information Available: X-ray crystallographic files for **2**, **4**, and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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