Carbon−Carbon Double Bond Formation Reactions of the Unique Spirocyclic Aluminum Bis(iminophosphorano) Methandiide Complex: Insertion of Heteroallenes into Aluminum−Carbon Bonds

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Received April 26, 2000

We recently reported both single and double deprotonation of the methylene backbone of bis(iminophosphorano)methane ligands to give methanide and bimetallic methandiide complexes of aluminum[1] which extended the application of this ligand system to this element. The latter bimetallic methandiide species contains a novel and unusual spirocyclic bridging carbene center. The reactivity of this novel dimetalated bridging carbene center was of interest particularly as this complex represents a new type of carbon center derivatized by aluminum. There has been recent growth of interest in aluminum complexes[2−11] themselves as single species catalysts for the polymerization of olefins rather than as activators of the early[12] and late[12a,13] transition metal complexes because of the electrophilic nature of cationic organoaluminum compounds.

Insertion of unsaturated small molecules into the metal−carbon bond and the carbon homologation reaction are fundamental steps in homogeneous catalysis. Although numerous reports on reactivity studies of transition metal complexes containing metal−carbon bonds with various small molecules exist,[14] similar studies on aluminum complexes are limited.[15−17] Here we describe the reactivity of our spirocyclic dimethyl aluminum bis(iminophosphorano)methandiide complex[1] with heteroallenes to form novel metallobicyclic compounds through a new C═C bond formation reaction.

Aluminum bis(iminophosphorano)methandiide, $[(\mathrm{AlMe_2})_2\{\mu_2\text{−}\mathrm{C(Ph_2P{=}NSiMe_3)_2}\text{-}\kappa C, \kappa C, \kappa N, \kappa N'\}]$, **1**, reacted with adamantylisocyanate under reflux conditions in toluene to yield $[(\mathrm{AlMe_2})_2\{(\mathrm{Me_3SiN{=}PPh_2})_2\mathrm{C{=}C(O)N(Ad)}\text{-}\kappa O,\kappa N,\kappa N',\kappa N''\}]$, **2** (Scheme 1).[18] Similarly, **1** reacted with dicyclohexylcarbodiimide to give $[(\mathrm{AlMe_2})_2\{(\mathrm{Me_3SiN{=}PPh_2})_2\mathrm{C{=}C(NCy)_2}\text{-}\kappa N,\kappa N',\kappa N'',\kappa N'''\}]$, **3**, (Scheme 1).[19] In both cases, an excess of the heteroallene gave neither further homologation reactions nor additional insertion into, for example, the Al−Me bond. This pattern is parallel to the behaviour of a related zinc complex reported earlier.[20] The ^{31}P NMR of the final reaction mixtures confirmed quantitative conversion of **1** to **2** or **3**. The complexes were isolated as a colorless air-sensitive crystalline solids in high yields.

This reaction in which two aluminum−carbon bonds are cleaved by one molecule of heteroallene to form new carbon−carbon double bonds in a novel bicyclic six-membered ring compounds is unique. Previous work shows that heteroallenes generally react with compounds containing metal−carbon bonds to give carboxylato-type derivatives.[21]

As expected, because complex **2** is not symmetric, the two inequivalent phosphorus centers give rise to two doublets in the

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(18) Preparation of **2**. (All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox.) $[(\mathrm{AlMe_2})\{\mu_2\text{−}\mathrm{C(Ph_2P{=}NSiMe_3)_2}\text{-}\kappa C, \kappa C, \kappa N, \kappa N'\}]$ **1** (0.20 g, 0.30 mmol) and adamantylisocyanate (0.053 g, 0.30 mmol) were dissolved in toluene (10 mL) and heated at 120 °C for 24 h. The resultant solution was concentrated to one-third of the original volume, and the flask was left at rt for 2 days. Colorless crystals were obtained which were filtered and dried under vacuum. Yield 0.18 g, 71.2%. IR data (Nujol Mull): 1348s, 1340s, 1304m, 1268m, 1252s, 1190w, 1138w, 1109s, 1052s, 1031m, 1014s, 1000m, 922w, 852s, 788m, 762m, 750m, 741m, 713m, 694s, 659m, 601w, 532m. ^{1}H NMR (C_6D_6): δ 7.60 (m, Ph), 7.39 (m, Ph), 6.90 (m, Ph), 6.68 (m, Ph), 2.14 (s, CH_2−Ad), 1.92 (s, CH−Ad), 1.53 (br dd, CH_2-Ad), 0.12 (s, CH_3−Al), 0.09 (s, CH_3Si), −0.0.2 (s, CH_3Si), −0.09 (s, CH_3−Al). ^{13}C {^{1}H} NMR (C_6D_6): δ 178.8 (br s, C−O), 134.0 (m, *o*-phenyl), 133.8 (m, *o*-phenyl), 133.3 (m, *i*-phenyl), 132.9 (m, *i*-phenyl), 131.8 (d, *p*-phenyl), 131.3 (d, *p*-phenyl), 128.3 (m, *m*-phenyl), 128.0 (m, *m*-phenyl), 58.5 (s, C.-Ad), 55.9 (dd, P−C−P, $^1J_{PC}$ = 128 Hz, 123 Hz), 42.3 (s, CH_2−Ad), 36.7 (s, CH_2−Ad), 30.5 (s, CH−Ad), 4.7 (s, CH_3Si), 3.7 (s, CH_3Si), 0.9 (s, CH_3−Al), −5.3 (s, CH_3−Al). ^{31}P{^{1}H} NMR (C_6D_6): δ 31.6 (d), 28.97 (d) $^2J_{pp}$ = 61.5 Hz. Anal. Calcd for $C_{46}H_{65}Al_2N_3OP_2Si_2$: C, 65.14; H, 7.72; N, 4.95. Found: C, 65.09; H, 7.89; N, 4.84.

(19) Preparation of **3**: In a fashion analogous to the preparation of **2**, dicyclohexylcarbodiimide (0.046 g, 0.22 mmol) was combined with **1** (0.15 g, 0.22 mmol). Yield 0.15 g, 73.9%. IR data (Nujol Mull): 1438s, 1357s, 1332s, 1296s, 1269s, 1251s, 1188s, 1111s, 1088s, 1071m, 1034s, 999m, 962m, 902s, 891m, 850s, 821m, 783s, 742s, 716m, 685s, 652s, 600s, 577m, 533s, 497s. ^{1}H NMR (C_6D_6): δ 8.44 (m, Ph), 7.37 (m, Ph), 7.29 (m, Ph), 7.12 (m, toluene), 7.03 (m, toluene), 6.38 (m, Ph), 6.26 (br, Ph), 5.97 (br, Ph), 3.60 (br s, *i*-Cy), 2.26 (br m, Cy), 2.10 (s, toluene), 1.73 (br s, Cy), 1.47 (m, Cy), 1.21 (m, Cy), 1.04 (m, Cy), 0.73 (m, Cy), 0.39 (s, CH_3Si), −0.03 (s, CH_3−Al), −0.21 (s, CH_3−Al). ^{13}C{^{1}H} NMR (C_6D_6): 187.8 (br t, C═C, $^2J_{PC}$ = 4.7 Hz), 137.8 (s, Tol), 136.5 (m, *o*-Ph), 135.0 (m, *i*-Ph), 133.6 (m, *o*-Ph), 132.6 (m, *o*-Ph), 132.0 (s, *p*-Ph), 131.3 (s, *p*-Ph), 131.2 (m, *i*-Ph), 129.3 (s, Tol), 129.0 (m, *m*-Ph), 128.5 (s, Tol), 125.6 (Tol), 65.0 (t, P−C−P, $^1J_{PC}$ = 106 Hz), 64.2 (s, CH−Cy), 33.5 (s, CH_2−Cy), 32.8 (s, CH_2−Cy), 27.4 (s, CH_2−Cy), 26.1 (s, CH_2−Cy), 21.4 (s, Me−Tol), 4.8 (s, $SiMe_3$), 0.6 (br s, Al−Me), −3.4 (br s, Al−Me). ^{31}P{^{1}H} NMR (C_6D_6): δ 30.15 (s). Anal. Calcd for **3**·toluene $C_{48}H_{72}Al_2N_4P_2Si_2$: C, 68.15; H, 8.32; N, 5.78. Found: C, 67.85; H, 8.45; N, 5.64.

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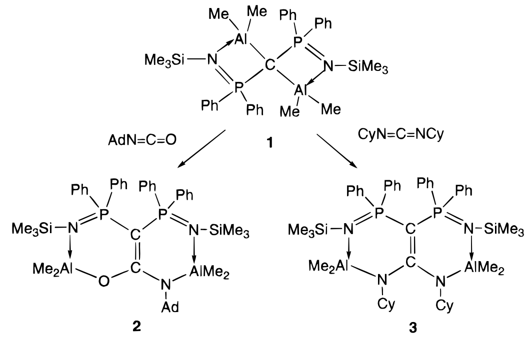
10.1021/ja001445q CCC: $19.00

Scheme 1



^{31}P NMR spectrum. The ^{13}C APT NMR spectrum for the backbone P−C−P carbon center appeared as a positive doublet of doublets, confirming the presence of the two non-equivalent phosphorus atoms. Proton and carbon NMR spectra for **2** also showed the expected two sets of Al−Me, phenyl, and $SiMe_3$ group resonances. The isocyanate carbon was observed as a broad singlet at 178.8 ppm. The phosphorus NMR spectrum of **3** shows only one singlet because both of the phosphorus atoms are equivalent in this symmetric molecule. Accordingly also the ^{13}C APT carbon signal of the P−C−P unit appeared as a positive triplet because of the coupling of this center with two equivalent phosphorus atoms. Surprisingly, however, complex **3** displayed two sets of Al−Me and phenyl resonances in both proton and carbon NMR; thus, the molecule must preserve the a boat conformation of metallocylic rings indicated in the crystal structure (vide infra) in solution. The two equatorial phenyl rings show two separate ortho and meta carbon resonances (as broad signals) probably because of the restricted rotation about the P−Ph bond.

The molecular structures of both **2**[22] and **3**[23] were confirmed by X-ray crystallography. An ORTEP[24] plot of the core structure of **3** is illustrated in Figure 1. The molecular structure shows two six-membered metallocyclic rings sharing an edge and adopting a distorted boat conformation in which the newly constructed ligand bridges the two dimethyl aluminum centers. In both the complexes the ligand therefore acts as a dianionic tetradentate ligand, and the aluminum atoms adopt a distorted tetrahedral geometry. Thus, in each case insertion of the heteroallene yields a new carbon−carbon double bond, the only difference being that in one heterocycle, **2**, an oxygen atom replaces one of the two NCy units seen in **3**. The C(1),C(2), P(1), P(2), N(3), N(4) atoms in complex **3** lie in one plane (Figure 1b) as do likewise the corresponding atoms (C(1), C(2), N(3), O) in complex **2**. In complex **3** the Al(1), N(1), P(1), N(3) atoms and Al(2), N(2), P(2), N(4) atoms also lie in one plane. These planes make an angle of 46.55(7)° and 48.09(5)° with the central plane, respectively. The Al-nitrogen distances {Al(1)−N(3) and Al(2)−N(4)} are shorter than those to the nitrogens of the Al−phosphinimine units {Al(1)−N(1) and Al(2)−N(2)} distances indicating that the charge is more localized on the former atoms. In both complexes **2** and **3** the C(1)−C(2) bond is shorter than than the single bond and longer than the double bond. The Al−N and Al−O distances are shorter than dative bond lengths but longer than normal single bonds in comparison to other four coordinate Al−N and Al−O compounds.[25] The P═N bond distances are elongated, and the endocyclic P−C bond distances are shorter; however, the exocyclic P−C distances are unchanged compared to the values in the free ligand.[26] All of these factors suggest that there is electronic delocalization within the tetradentate dianionic ligand as represented in Scheme 2.

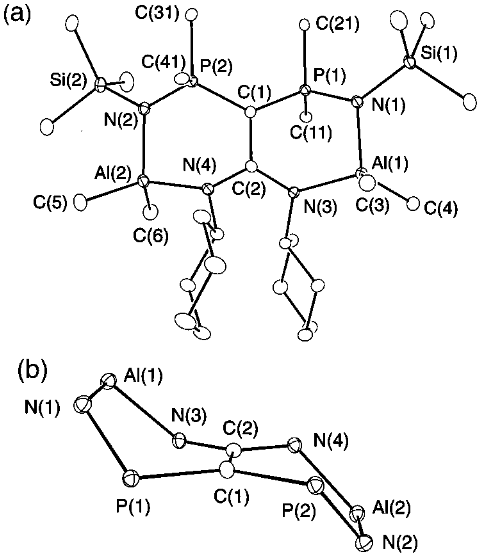
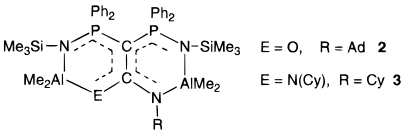


Figure 1. (a) An ORTEP[24] view of $[(AlMe_2)_2\{(Me_3SiN{=}PPh_2)_2C{=}C(NCy)_2\text{-}\kappa N,\kappa N',\kappa N'',\kappa N'''\}]$ **3** showing the atom labeling scheme. The hydrogen atoms and all but *ipso* carbon atoms of the phenyl groups have been removed for clarity. Remaining atoms are represented by Gaussian ellipsoids at the 20% probability level. Bond lengths and bond angles are given in ref 23. (b) An oblique view of the bicyclic frame of **3**.

Scheme 2



Summarizing, heteroallenes react with the spirocyclic dimethyl aluminum bis(iminophosphorano)methandiide complex to give novel bicyclic aluminum complexes in which a new carbon−carbon multiple bond is formed. These products also provide rare examples of aluminum bicyclic ring systems. Further reactivity studies are underway.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, NOVA Chemicals Ltd. of Calgary and the University of Alberta for financial support.

Supporting Information Available: Experimental details (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA001445Q

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[22] Crystal Data for **2**: Monoclinic, $P2_1/c$ (No. 14), $a = 10.6208(6)$ Å, $b = 18.2546(11)$ Å, $c = 24.4927(14)$ Å, $\beta = 100.6006(11)°$, V (Å^3) = 4667.6(5), $Z = 4$. The structure was solved by direct methods and refined by full matrix least squares procedures: $R_1 = 0.0412$ ($wR_2 = 0.1178$) for 6721 reflections with $F_o^2 \geq 2\sigma(F_o^2)$. Selected interatomic distances [Å] and angles [deg] for **2** are: Al(1)−N(1) = 1.928(2), Al(1)−O = 1.800(2), Al(1)−C(3) = 1.973(3), Al(2)−N(2) = 1.948(2), Al(2)−N(3) = 1.959(2), Al(2)−C(5) = 1.977(3), C(1)−C(2) = 1.442(3), N(1)−P(1) = 1.621(2), P(1)−C(1) = 1.768(2), P(2)−C(1) = 1.768(2), P(2)−N(2) = 1.614(2), N(1)−Al(1)-O = 96.57(8), N(2)−Al(2)-N(3) = 96.58(8), P(1)−C(1)-P(2) = 128.7(1).

[23] Crystal Data for **3**: Triclinic, $P\bar{1}$ (No.2), $a = 12.4477(9)$ Å, $b = 13.2048(9)$ Å, $c = 18.2357(13)$ Å, $\alpha = 91.0447(13)°$, $\beta = 101.9669(13)°$, $\gamma = 109.6232(12)°$, V (Å^3) = 2749.4(3), $Z = 2$. The structure was solved by direct methods and refined by full matrix least squares procedures: $R_1 = 0.0466$ ($wR_2 = 0.1428$) for 7937 reflections with $F_o^2 \geq 2\sigma(F_o^2)$.Selected interatomic distances [Å] and angles [deg] for **3** are: Al(1)−N(1) = 1.935(2), Al(1)−N(3) = 1.915(2), Al(2)−N(2) = 1.938(2), Al(2)−N(4) = 1.908(2), C(1)−C(2) = 1.456(3), N(1)−P(1) = 1.616(2), P(1)−C(1) = 1.769(2), P(2)−C(1) = 1.759(2), P(2)−N(2) = 1.624(2), N(1)−Al(1)-N(3) = 98.54(8), N(2)−Al(2)-N(4) = 98.53(8), P(1)−C(1)-P(2) = 132.2(1), N(3)−C(2)-N(4) = 123.6(2).

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