# Incorporation of a Complexed AlH Fragment into a Metallacycle. Preparation and Characterization of $CpCoC_4Ph_4AlH{\cdot}NEt_3$[†]

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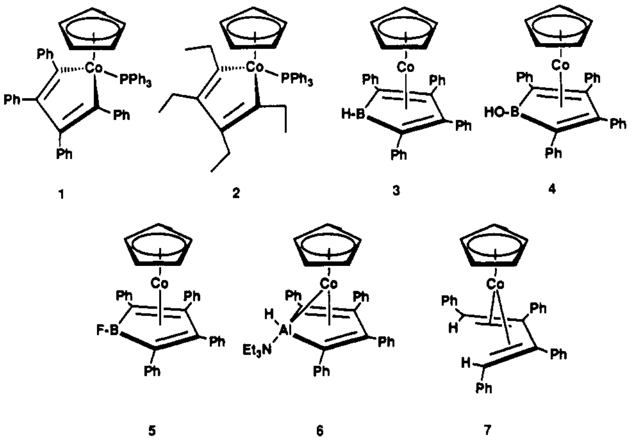
The reaction of $Cp(PPh_3)\overline{CoCPhCPhCPhC}Ph$ with $AlH_3{\cdot}NEt_3$ proceeds smoothly at elevated temperatures to produce $CpCoC_4Ph_4AlH{\cdot}NEt_3$ (6) in 80% isolated yield. The composition and proposed structure is based on $^1H$, $^{13}C$, and $^{27}Al$ NMR, IR, and other data. The green compound is extremely water sensitive and modestly sensitive to oxygen. Hydrolysis leads to quantitative formation of $CpCo(\eta^4\text{-}C_4Ph_4H_2)$ (7). Addition of $Et_2OBF_3$ leads to a 60% isolated yield of $CpCo(\eta^5\text{-}C_4Ph_4BF)$ (5), which has been fully characterized spectroscopically. The $CpCo(\eta^5\text{-}C_4Ph_4BF)$ derivative reacts with $H^-$ to yield primarily $CpCo(\eta^5\text{-}C_4Ph_4BH)$ (3). Reaction with propylene results in the rapid destruction of $CpCoC_4Ph_4AlH{\cdot}NEt_3$ with the concomitant loss of ≈10 propylene molecules. However, the intractable products could not be characterized.

## Introduction

The chemistry of boron differs in many respects from that of the other group 13 elements. Indeed, it might be said that similarities are less common than differences. Hence, there is significant interest in putting aluminum into a bonding environment similar to that found in boron chemistry in order to see how it behaves. In fact, examples of aluminaboranes,[1] aluminacarboranes,[2] and transition-metal–aluminum hydride complexes[3] have been known for some time[4] but recently significant new advances have been reported. Hawthorne et al. have synthesized a variety of group 13 element metallacarboranes and have described their structures and reactivity.[5] Sneddon et al. have reported the incorporation of $Et_3N{\cdot}AlH_x$, $x = 1, 2$, into smaller carboranes by the reaction of $Et_3N{\cdot}AlH_3$ with *nido*-2,3-$Et_2C_2B_4H_6$.[6] Further, Shore et al have reported the synthesis and structural characterization of *closo*-$[B_{11}H_{11}AlMe]^{2-}$, which is an analogue of the *closo*-$[B_{12}H_{12}]^{2-}$ dianion.[7] The boron matrix, as it were, provides guidance in the synthesis of these compounds as well as in understanding their structure and bonding.

There has also been great emphasis in recent years on the stabilization of main-group elements in unusual bonding modes.[8] An effective approach has been the use of bulky substituents, often on the main-group atom, to kinetically and/or thermodynamically inhibit degradative reactions. However, in doing so the reactivity of the main-group center can be lost. An alternative approach is to stabilize the main-group moiety via incorporation into an organometallic fragment.[9] Here reactivity is modified but large steric barriers need not be present. Thus, in our variation of this approach the reaction of a metallacycle with $BH_nCl_{3-n}{\cdot}L$, $n = 1, 2$, leads to the incorporation of a BH fragment to yield a metallacarborane, $CpCo(\eta^5\text{-}C_4Ph_4BH)$ (3), as the principal final product.[10] Compared to that of other compounds containing a BH fragment, the reactivity of the BH fragment in 3 is considerably modified by its environment. It is noteworthy that an analogous (isolobal) preparative route yields $CpCo(\eta^5\text{-}C_4Ph_4Fe(CO)_3)$.[11] In principle, the strategy should work with other main-group E–H fragments. Thus, we have now explored this approach to an aluminum system in an attempt to synthesis $CpCo(\eta^5\text{-}C_4Ph_4AlH)$.

Chart I



Aluminoles have been known for some time[12] and there is a characterized example of a nickel complex similar to

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[†] Dedicated to Prof. John J. Eisch on the occasion of his 60th birthday.

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(8) See for example: Bartlett, R. A.; Dias, H. V. R.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 1306.

(9) See, for example: Huttner, G.; Sigwarth, B.; Scheidsteger, O.; Zsolnai, L.; Orama, O. *Organometallics* **1985**, *4*, 326.

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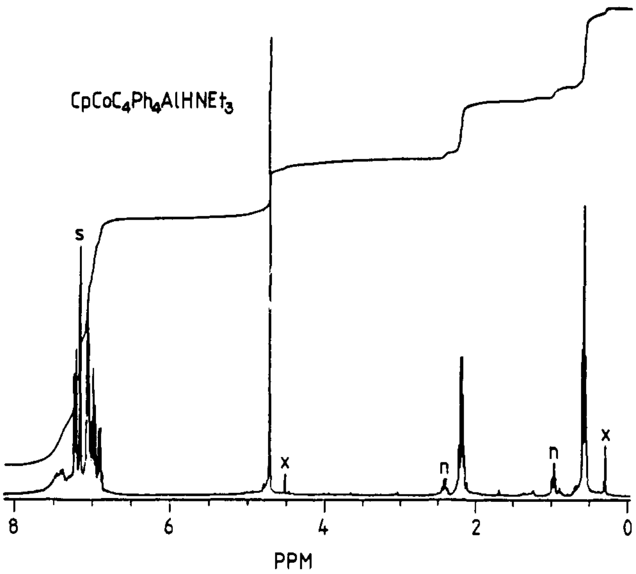


**Figure 1.** The 300-MHz $^1$H NMR spectrum of $\mathrm{CpCoC_4Ph_4AlH{\cdot}NEt_3}$ (**6**) in $\mathrm{C_6D_6}$ at 22 °C. The resonances labeled s, n, and x are due to solvent, an amine alane impurity (see text), and unknown impurities, respectively.

our target molecule, i.e., CODNi($\eta^4$-$\mathrm{C_4Ph_4AlPh{\cdot}OEt_2}$).[13] This compound contains an Al–Ph fragment rather than Al–H and is prepared from the aluminole itself and a source of the NiCOD fragment. Hence, our approach potentially provides an alternative route to such compounds. Importantly, CpCo($\eta^5$-$\mathrm{C_4Ph_4AlH}$) would allow the reactivity of an Al–H bond in a new environment to be characterized. Based on our observations of **3**, we except the Al–H bond in CpCo($\eta^5$-$\mathrm{C_4Ph_4AlH}$) to be less active than that in other aluminum hydrides but much more active than the B–H fragment in **3**.

## Results

**Preparation and Characterization of $\mathrm{CpCoC_4Ph_4AlH{\cdot}NEt_3}$ (6).** The attempted preparation of CpCo($\eta^5$-$\mathrm{C_4Ph_4AlH}$) from the reaction of $\mathrm{Et_3N{\cdot}AlH_3}$ and $\mathrm{Cp(PPh_3)\overline{CoCPhCPhCPhC}Ph}$ (**1**) led to the formation of the amine adduct $\mathrm{CpCoC_4Ph_4AlH{\cdot}NEt_3}$ (**6**) according to reaction 1. The overall yield of **6** (≈80%) was considerably

$$\mathrm{Cp(PPh_3)\overline{CoCPhCPhCPhC}Ph + Et_3N{\cdot}AlH_3 \rightarrow CpCoC_4Ph_4AlH{\cdot}NEt_3 + PPh_3 + H_2} \quad (1)$$

higher than that for the formation of **3** by a similar route. Indeed chromatography on **6** was not possible and the high yield permitted the removal of the coproduct, $\mathrm{PPh_3}$, by fractional crystallization. Unfortunately, although **6** was isolated as a reasonably pure, green, air- and water-sensitive oil, crystals suitable for X-ray structure determination have not been forthcoming despite many attempts at growing them. The utilization of $\mathrm{(C_6H_{11})_2(CH_3)N{\cdot}AlH_3}$ in the hope of obtaining a more easily crystallizable material did not give as clean a preparative reaction and purification was not possible. The product **6** consistently contained ≈5% of an amine alane derivative, possibly a triethylamine polyalane adduct.[14] Because of the more active Al–H of this impurity, its presence made the characterization of the reactivity of **6** more difficult.

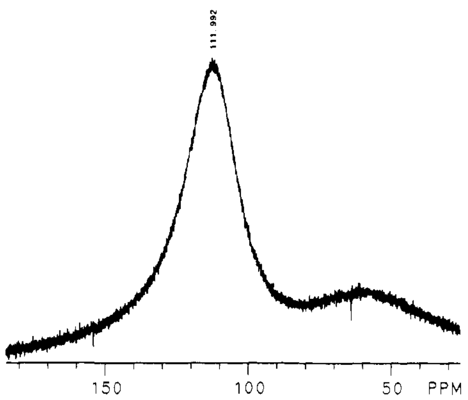


**Figure 2.** The 78.2-MHz $^{27}$Al NMR spectrum of $\mathrm{CpCoC_4Ph_4AlH{\cdot}NEt_3}$ (**6**) in $\mathrm{C_6D_6}$ at 22 °C. The very broad resonance at $\delta$ 60 is due to aluminum in the probe.

Chart II

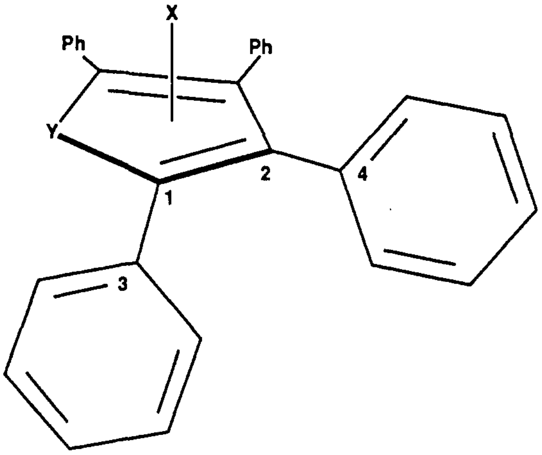
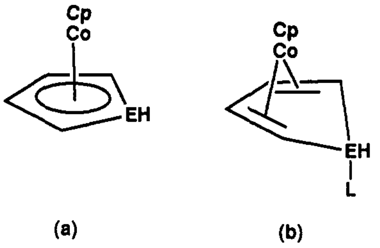


Chart III



(a) (b)

We were only able to obtain the composition of $\mathrm{CpCoC_4Ph_4AlH{\cdot}NEt_3}$ (**6**) indirectly, as mass spectrometry of the purified product consistently showed only the product of hydrolysis. The multinuclear NMR experiments demonstrate the presence of C, H, Al, and the structural units of one Cp, four Ph, three Et (as $\mathrm{NEt_3}$), and one AlH. The $^1$H and $^{27}$Al NMR spectra are shown in Figures 1 and 2 and assignments and chemical shifts for selected resonances of the $^1$H and $^{13}$C spectra are given in Table I. The assignment of the $^1$H data was straightforward. For the $^{13}$C NMR measurements, $^{13}$C–$^1$H coupled spectra with NOE recorded in the 1PDFA mode were used to aid assignment. Carbon C(I) (Chart II) was too weak or broad to be observed for compounds **3**–**6** in these experiments. The reported $^{13}$C spectrum of a nickelole analogue also aided the assignments for **1** and **2**.[15] The chemical shift of the AlH proton is similar to that reported

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**Table I. Selected $^1H$ and $^{13}C$ NMR Data**

| | $1^a$ | $2^a$ | $3^a$ | $4^a$ | $5^a$ | $6^a$ | $7^a$ |
|---|---|---|---|---|---|---|---|
| | | | | $^1H$ NMR | | | |
| $C_5H_5$ | 4.78 | 4.94 | 4.42 | 4.43 | 4.40 | 4.70 | 4.51 |
| | | | | $^{13}C$ NMR | | | |
| $C_5H_5$ | 89.95 | 87.29 | 83.88 | 84.38 | 84.51 | 83.58 | 84.52 |
| $^1J$ | 176.3 | 174.2 | 178.3 | 177.0 | 178.3 | 175.3 | 176.1 |
| $^2J$ | 5.2 | 7.1 | 6.7 | 6.8 | 6.7 | 6.7 | 6.7 |
| mult | d/qnt | d/qnt | d/qnt | d/qnt | d/qnt | d/qnt | d/qnt |
| C(1) | 167.68 | 163.75 | | | | | 52.78 |
| $J$(C–P) | 28.72 | 37.8 | | | | | |
| $^1J$ | | | | | | | 155.22 |
| $^2J$ | | | | | | | 4.2 |
| C(2) | 158.45 | 155.25 | 104.59 | 99.45 | 99.01 | 105.15 | 96.46 |
| $J$(C–P) | 2.6 | 3.2 | | | | | |
| $^1J$ | | 0 | 0 | 0 | 0 | 0 | |
| $^2J$ | | 8.26 | 2.1 | 2.0 | 2.8 | 3.0 | 2 |
| mult | | s/d | s/t | s/t (br) | s/t (br) | s/t | s/m (br) |
| C(3) | 142.57 | 23.31 | 141.70 | 140.86 | 139.43 | 141.77 | 145.01 |
| $J$(C–X) | 3.1 (P) | 3.3 (P) | | | 2 (F) | | |
| $^1J$ | | 122 | 0 | 0 | | 0 | 0 |
| $^2J$ | | | 6.3 | 6.2 | | 5.6 | 6.1 |
| mult | s/m | t/– | s/t (br) | s/t | d | s/t (br) | s/m |
| C(4) | 154.17 | 35.57 | 136.61 | 136.48 | 135.88 | 150.48 | 137.96 |
| $^1J$ | 0 | 122.4 | 0 | 0 | 0 | 0 | 0 |
| $^2J$ | 7.33 | 0 | 7.8 | 7.6 | 7.0 | 7.2 | |
| mult | s/m | t/– | s/t | s/t | s/t | s/t | s/m |

[a] See Chart I for structures and Chart II for carbon labeling.

for terminal hydrides found in transition-metal aluminohydride complexes.[3] Mass spectrometry and quantitative hydrolysis showed the presence of the $CpCoC_4Ph_4$ fragment in 6. Finally, the IR and the $^{27}Al$ NMR spectra (Al–H coupling) corroborated the presence of an AlH fragment. Hence, the formulation as $CpCoC_4Ph_4AlH \cdot NEt_3$.

The structure presents an interesting puzzle given that the compound contains the fragments CpCo, $C_4Ph_4$, AlH, and $NEt_3$. If one treats the compound as a Co(I) derivative, earlier discussions of base adducts of the related boron compounds[16] would suggest the structure shown in part b rather than that of part a in Chart III which is found for $CpCo(\eta^5\text{-}C_4Ph_4BH)$ and other closely related compounds. The $^{13}C$ NMR data of 6 as well as those of several related compounds are given in Table I. These data show the presence of a plane of symmetry in 6 and the $^{13}C$ chemical shifts of the Cp and C(2) carbons are consistent with the structure in Chart IIIb. The chemical shift of the Cp ligand in the $^1H$ NMR spectrum and those of C(3) and C(4) in the $^{13}C$ NMR spectrum, however, make one uneasy with this assignment. In both cases these shifts suggest environments similar to those in a metallacycle, e.g., 1, rather than of compounds containing diene and $\pi$ ligands. But most telling is the fact that CpCo compounds containing diene and polyhapto $\pi$ ligands are usually red and yellow/orange, respectively, thereby making the green color of 6 completely unexplained.

Taking a cluster rather than metal–ligand point of view provides alternative structures to the single one shown in Chart III. The six-vertex cluster $CpCoC_4Ph_4AlH \cdot NEt_3$ has a formal SEP count of nine pair, and, hence, according to Wade's rules[17,18] the structure should be based on a dodecahedron with two vacant vertices. As shown in Figure 3, more then one structure containing a plane of symmetry can be generated. Structure **6b** is the same as that in Chart IIIb while structure **6a** is a benzvalene structure that has previously been suggested as the structure of the transition state for the skeletal rearrangement of compounds like **3**.[19] The existence of an aluminum–cobalt interaction in **6a** could give rise to the different absorption properties of the cobalt center and this assignment gives a better fit to the $^1H$ chemical shift for Cp and the $^{13}C$ chemical shift for C(4). However, the $^{13}C$ chemical shift of the C(2) carbon is 30–40 ppm further upfield than one would expect for carbons involved in the localized double bond that must be present in **6a**. Thus, this structure is ruled out.

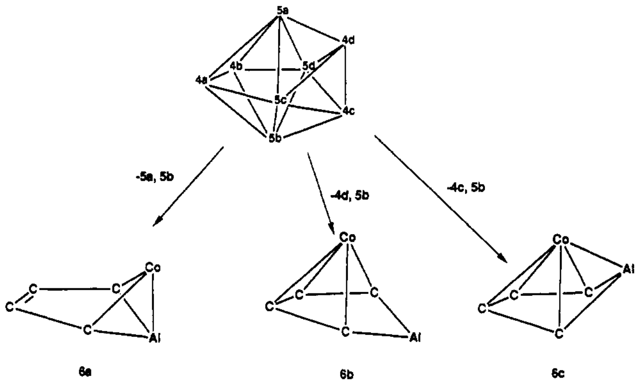
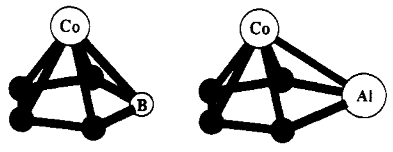


**Figure 3.** Three ways of generating an arachno six-atom cluster from a dodecahedron by removal of four- or five-coordinate vertices such that the resulting core retains a plane of symmetry.



3 6

**Figure 4.** Scale representations of the cage skeletons for $CpCo(\eta^5\text{-}C_4Ph_4BH)$ (**3**) and $CpCoC_4Ph_4AlH \cdot NEt_3$ (**6**). In the latter case of $CoC_4$ unit is taken from the known structure of the boron derivative[10] and the Al–C and Al–Co distances are fixed at the sum of the covalent radii (1.98 and 2.45 Å).

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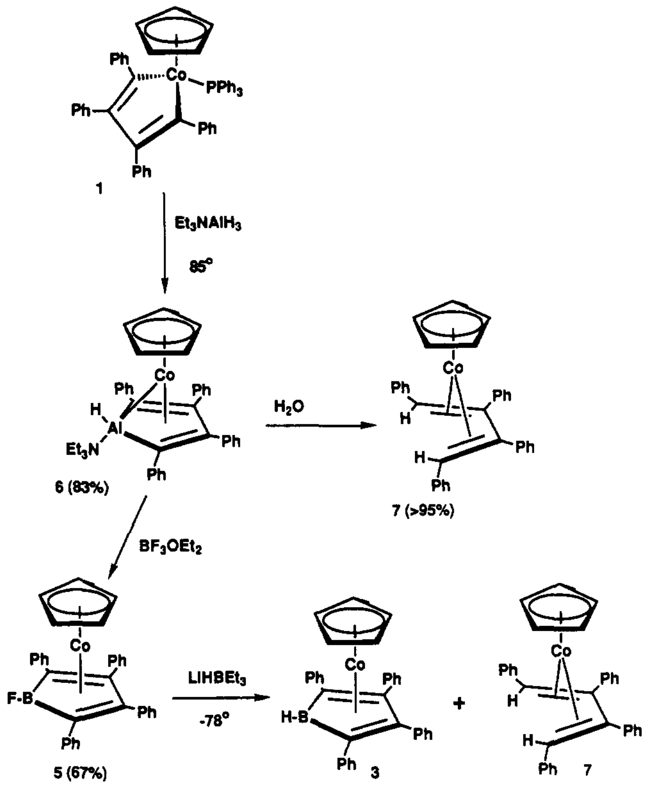

**Figure 5.** Schematic representation of the reactivity of $CpCoC_4Ph_4AlH{\cdot}NEt_3$ (6).

This leaves us with structure **6c**. Again there is a direct aluminum–cobalt interaction that can be used to account for the unusual color of **6**. The connectivity of structure **6c** is actually the same as that in Chart IIIa and the $^{13}C$ chemical shifts for C(2), C(3), and Cp are very similar to those of compound **3**. However, the $^{1}H$ chemical shift for Cp and the $^{13}C$ chemical shift for C(4) still suggest that the cobalt fragment interacts with the tetraphenyl butadiene fragment in a manner similar to that in **1** and **2**.

Both structures **6a** and **6c** have five-coordinate aluminum atoms while that of **6b** is four coordinate. Hence, it is of interest to look at the $^{27}Al$ NMR more closely.[3,20] It has been reported that the chemical shifts of compounds containing authenic five-coordinate aluminum lie in the range δ 112–126, e.g., $[Me_2AlO(CH_2)_2OMe]_2$.[21] These resonances are independent of temperature.[22] The chemical shift observed for **6** is in this range but the line width observed (1360 Hz) is somewhat less than the 2500–8000-Hz range reported earlier.[23] We conclude that the $^{27}Al$ NMR spectrum is consistent with structures **6a** and **6c** but does not exclude structure **6b**.

**Selected Reactions of $CpCoC_4Ph_4AlH{\cdot}NEt_3$ (6).** The three reactions of **6**, reported immediately below, as well as the preparative reaction already mentioned above, are summarized in Figure 5. The hydrolysis reaction, used already as a chemical proof of stoichiometry, is quantitative by $^{1}H$ NMR. The characteristic green to red color change that indicates hydrolysis of **6** to **7** takes place in ca. 15 min for a solution of the pure compound under an atmosphere of standard tank nitrogen. The reaction mixture, which contains excess $Et_3OAlH_3$, is stable under these conditions; however, hydrolysis is complete when purification is attempted on a short silica gel column. For these reasons, compound **6** was handled under a purified argon atmosphere or under vacuum.

In attempt to remove the coordinated $NEt_3$ from **6**, the reaction of $Et_2OBF_3$ with **6** was investigated, as $BF_3$ was expected to serve as a strong sequestering agent for the amine. With an excess of $Et_2OBF_3$, an orange solid product was isolated in good yield. The identity of this material as the fluorine derivative of compound **3**, namely, $CpCo(\eta^5\text{-}C_4Ph_4BF)$ (**5**), is clear from its spectroscopic properties. The proposed structure of **5**, analogous to that known for **3**, is indicated in Chart I. In order to provide more insight on a rather unusual transformation, we examined the course of reaction 2 by $^{1}H$ NMR spectroscopy. In doing

$$Et_2OBF_3 + CpCoC_4Ph_4AlH{\cdot}NEt_3 \rightarrow CpCo(\eta^5\text{-}C_4Ph_4BF) \qquad (2)$$

so a complication from the unknown alane impurity (see above and Figure 1) was revealed. Using integrated intensities as a measure of concentrations, we found that for each mole of the amine associated with this impurity a fraction of **6** was destroyed; i.e., the total Cp signal decreased in the first 5 min of the reaction (10–60% depending on whether the impurity level was low or high) without the formation of **5**. The destruction of **6** by sources of uncoordinated aluminum hydride was confirmed by carrying out a similar reaction with a mixture of $Et_3NAlH_3$ and **6**. Adding less than 1 mol of $Et_2OBF_3$ per mole of $Et_3NAlH_3$ led to the destruction of a fraction of **6** but no production of **5**.

In reaction 2, after the known alane impurity was gone as evidenced by the shift of its characteristic amine signal to a chemical shift corresponding to that of $Et_3NBF_3$, the Cp signals showed a smooth evolution of **5** and concurrent loss of **6**. Small amounts of **3** and **7** appeared as byproducts and a minor unknown product with a Cp signal at δ 4.66 was also produced. The time behavior of the Cp signals observed suggests that there are no intermediates of significant stability under the reaction conditions. Despite its complexity then, reaction 2 exhibits no prominent intermediates under the reaction conditions and the reaction mechanism remains obscure.

The presence of **3** and **7** as byproducts of reaction 2 was puzzling and we suspected that the hydride impurity might play a role in their formation as well. This was confirmed by showing that the reaction of **5** with $NaHBEt_3$ yielded mainly **3** but some **7** as products. Thus, the byproducts in the reaction of **6** with $Et_2OBF_3$ presumably result from the reaction of some residual hydride impurity with the major product **5**. It appears, then, if we could completely remove the alane impurities from **6**, the overall yield for the production of **5** would be even higher than the ≈70% observed.

We noted that it was necessary to remove all traces of unsaturated compounds from the hexanes before they could be used as solvents for **6**. Thus, we investigated the controlled reaction of **6** with an olefin, i.e., propylene. Reaction at room temperature or at −20 °C was catalytic in **6**, giving turnover numbers of about 70 (reaction time 15 h) and 20 (reaction time 60 h), respectively, based on consumption of propylene. If the initially rapid uptake of propylene is neglected, a plot of $\ln(1 - \Delta P/P_0)$ versus $t$, where $\Delta P$ is the pressure change at time $t$ and $P_0$ is the initial pressure of propylene, is a straight line, e.g., slope of $3 \times 10^{-5}$ m$^{-1}$ at −20 °C ($R = 0.96$). The initial, rapid consumption of propylene was 14 and 15 mol of propylene/mol of **6** at room temperature and −20 °C, respectively.

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The insoluble product produced exhibited a C/H analysis showing that, if polypropylene is being formed, it is very impure. Finally, in the early stages of the reaction the green solution turned pale red.

We also examined this reaction using $^1$H NMR as a probe. On the addition of propylene, **6** is very rapidly consumed producing 1 mol of what appears to be the impurity alane (based on the chemical shift of the coordinated $NEt_3$, $\delta$ 2.43 q, 0.93 t) per mole of **6** lost. As compound **7** is not a product of this reaction, and, as the Cp signal of **6** lost is not replaced by signals from any other compounds, we assume the product produced from **6** is removed from solution in some fashion. Thus, it is clear that the active species causing consumption of propylene after 1 h is not **6** and that the solid produced after the demise of **6** contains a species generated from **6** and, possibly, polypropylene.

## Discussion

Taking structure **6c** as the most likely structure for $CpCoC_4Ph_4AlH{\cdot}NEt_3$, the product of reaction 1, we can construct a geometric representation of the essential core by using the structural data for compound **3**. This is shown in Figure 4 and one notes the qualitative similarity between the two structures. The suggested structure of **6** is similar to that of CODNi($\eta^4$-$C_4Ph_4AlPh{\cdot}OEt_2$),[10] as one might expect. In **6** we have used a Co–Al distance of 2.45 Å (covalent radius of Al = 1.18 Å), while the nickel analogue has a Ni–Al distance of 2.748 (1) Å. The authors consider this a bonding distance, based on their chosen covalent radius for Al (1.43 Å) and other structural changes that take place on coordination of the aluminole to the nickel center. The rather large range of covalent radii published for Al[24] means that **6** could have the aluminum atom lying above the plane defined by the four ring carbon atoms as shown in Figure 4 or below the plane as exhibited by the nickel analogue, while still having a direct bonding interaction between the transition metal and the aluminum atom.

The high reactivity of $CpCoC_4Ph_4AlH{\cdot}NEt_3$ (**6**) coupled with its good solubility in organic solvents makes it a potentially useful reagent for transmetalation. This has already been accomplished with use of an aluminacarborane in the synthesis of other metallacarboranes[25] and our unexpected observation of the conversion of **6** to **5** with $Et_2OBF_3$ provides another example. However, the factors controlling the pathways leading to elimination of aluminum to form **7** and replacement to form **5** are not understood at this point. Further, the rapid reaction of **6** with propylene, with the consumption of ≥10 mol per mol of **6**, suggests catalytic activity for polymerization but **6** has a very short lifetime under the reaction conditions. Unfortunately, the product of the reaction of **6** with an olefin appears intractable. It is interesting to note, however, that $CpCoC_4Ph_4AlH{\cdot}NEt_3$ in itself meets the requirements of a known type of olefin polymerization catalyst, namely, that it contains cobalt metal and an active hydride.[26,27] In the previous work, the catalytic activity was attributed to a $\pi$-allylic derivative formed from a cobalt hydride and the olefin.

## Experimental Section

All reactions and manipulations were carried out with standard Schlenk apparatus in a dry argon atmosphere or a high-vacuum line.[28] Solvents were purified according to standard procedures (hexanes, pentane, and toluene were first washed with concentrated $H_2SO_4$ and then rinsed with distilled water followed by $NaHCO_3$ before drying over KOH pellets), degassed, and distilled from sodium benzophenone ketyl before use. The ethanol used was degassed over a wide frit with nitrogen. $CoCl_2{\cdot}xH_2O$, Zn dust, $LiAlH_4$, $Et_3N{\cdot}HCl$, 2 M NaCp in THF, $BF_3{\cdot}OEt_2$, $NaHBEt_3$, $Et_3N$, and $PPh_3$ were used as received (Aldrich). Propene (Matheson) was dried by passage through a column packed with $P_2O_5$. Solids were degassed under vacuum before use.

IR spectra were recorded in a $CaF_2$ cell on a Perkin-Elmer 1420 spectrophotometer calibrated by using the polystyrene band at 1601 cm$^{-1}$. $^{11}$B ($BF_3{\cdot}OEt_2$, $\delta = 0$) and $^{27}$Al ($(Al(OH)_6{}^{3+}$, $\delta = 0$) NMR were acquired on a Nicolet NT 300 spectrometer (96.3 and 78.2 MHz, respectively) while the $^1$H ($C_6D_6$, $\delta = 7.15$) and $^{13}$C ($C_6D_6$, $\delta = 128$) NMR spectra were recorded on either a Magnachem A200 (200 and 50.5 MHz, respectively) or a General Electric GN 300 (300 and 75.6 MHz, respectively) spectrometer. Mass spectdra were obtained with a Finnigan MAT 8450 high-resolution mass spectrometer in the EI or CI mode. A Carle Model 311 gas chromatograph with molecular sieves and Porapak columns in series and argon carrier gas was used to identify $H_2$.

The published procedures for the preparations of $Cp(PPh_3)\overline{CoCPhCPhCPhCPh}$ (**1**)[29] and $Et_3N{\cdot}AlH_3$ were used.[30]

**Preparation of $CpCoC_4Ph_4AlH{\cdot}NEt_3$ (6).** A 0.26-g (0.35 mmol) portion of pure, crystalline $Cp(PPh_3)\overline{CoCPhCPhCPhCPh}$ (**1**) was dissolved in 30 mL of toluene, giving a brown solution. Any undissolved solid was removed by filtration. To the solution was added 3 equiv (0.5 mL of 3.4 M) of $Et_3N{\cdot}AlH_3$ in $Et_2O$. The ether was removed under reduced pressure and the solution with a partial vacuum above it was tightly stoppered and heated to 85 °C for 9 h. The color turned a bright green. The cooled reaction mixture was brought up to atmospheric pressure with argon. Sampling the gas phase at this point showed the presence of $H_2$. To the product mixture was added 10 mL of hexanes. After standing overnight at 0 °C the mixture was filtered through a fine frit. A brown residue was discarded. The filtrate was stripped of solvent and left under high vacuum for 2 days to sublime off unreacted amine alane. The dry oil remaining was dissolved in 10 mL of toluene and 10 mL of pentane, cooled overnight, and filtered into a small preweighed Schlenk tube and stripped of solvent before drying under high vacuum for 24 h to give $CpCoC_4Ph_4AlH{\cdot}NEt_3$ (**6**) as a green oil in a yield of 0.174 g (83%). This material was pure apart from a ≈5% amine polyalane impurity, which we failed to remove. Because of contamination with both solvent and unknown alane impurity, elemental analysis was not attempted.

Repeated attempts to obtain a mass spectrum of the highest purity **6** with either EI or CI led to a predominant highest mass ion at $m/e$ 482, which corresponds to the mass of CpCo($\eta^4$-$C_4Ph_4H_2$) (**7**), the known product of hydrolysis. The mass spectrum of the reaction mixture containing both amine alane and $PPh_3$ under CI conditions did yield a high mass ion at $m/e$ 608 which is consistent with the p − 1 ion of **6**. The best analytical data we were able to obtain resulted from the hydrolysis of **6** to yield **7**. The Cp signal in the $^1$H NMR of the two compounds integrated with respect to an internal standard showed the formation of 0.97 mol of **7** per mole of **6** hydrolyzed.

IR ($C_6H_6$, 3500–1400 cm$^{-1}$) 3230 m, 3070 sh, 3050 m, 3020 sh, 2970 m, 2850 w, 2380 m, 2365 w, 2260 s, br, 1780 m, br, 1610 m, 1582 m, 1480 m, 1445 m, 1435 sh. On exposure to air, the band at 1780 cm$^{-1}$ is lost as the solution turns from green to red but there is little change in the other bands. $^1$H NMR ($C_6D_6$, 22 °C, $\delta$) 7.22–6.86 m (Ph, $I_{calc} = 20$, $I_{obs} = 27.8$), 4.9 br s (AlH, $I_{calc}$ 1, $I_{obs} = 0.7$), 4.710 s (Cp, $I_{calc} = 5$, $I_{obs} = 5$), 2.182 q ($CH_2$, $I_{calc} = 6$, $I_{obs} = 6.6$), 0.564 t ($CH_3$, $I_{calc} = 9$, $I_{obs} = 9.2$). For reference compare $Et_3{\cdot}AlH_3$ ($C_6D_6$, 22 °C, $\delta$) 4.0 br (AlH), 2.384 q ($CH_2$), 0.863 t ($CH_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 22 °C, $\delta$) 150.5 ($C_4$), 141.8 ($C_3$), 130.8 (Ph), 129–127 (obscured by solvent), 125.8 (Ph), 122.5 (Ph), 105.2 ($C_2$), 83.6 (Cp), 45.9 ($CH_3$), 8.4 ($CH_2$). $^{27}$Al NMR ($C_6D_6$, 22

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°C, δ ref to 0.5 M $Al(OH)_6^{3+}$), 112 br (FWHM 1360 Hz, {$^1$H} 1120 Hz).

**Reaction of $CpCoC_4Ph_4AlH{\cdot}NEt_3$ (6) with $Et_2OBF_3$.** Compound **6** was prepared from 0.77 g (1.04 mmol) of **1** according to the above procedure. A solution of **6** in about 15 mL of toluene was treated with 3 equiv (0.45 mL, 3.12 mmol) of $Et_2OBF_3$, and after 2 days stirring at room temperature, a white precipitate formed and the color changed from green to red. Ten milliliters of hexanes was added and the mixture allowed to sit for about 3 h. Filtration through a medium frit gave a red solution and a white residual, which was discarded. The solvent was vacuum stripped and the solid dried under vacuum. The yield of red-orange $CpCo(\eta^5\text{-}C_4Ph_4BF)$ (**5**) was 0.35 g (67%). MS, EI, $p^+$ = 512, one boron. $^{11}$B NMR (toluene, 22 °C, δ) 19.3 br (fwhm = 250 Hz). $^1$H NMR ($C_6D_6$, 22 °C) δ 7.22–6.86 m (Ph), 4.40 s (Cp). $^{13}$C{$^1$H} NMR ($C_6D_6$, 22 °C, δ) 139.4 ($C_3$), 135.9 ($C_4$), 134–125 (Ph, 129–127 obscured by solvent), 99.0 ($C_2$), 84.5 (Cp).

A 0.15-g (0.3 mmol) sample of **5** was dissolved in 3 mL of THF and cooled to −78 °C and 0.3 mL of 1 M $NaHBEt_3$ was added. After it was stirred for 1 h, the solution was allowed to warm to room temperature, the solvent was stripped off, and the $^1$H NMR spectrum was recorded in $C_6D_6$. The major product produced was compound **3** along with some compound **7**.

**Reaction of $CpCoC_4Ph_4AlH{\cdot}NEt_3$ (6) with Propene.** A solution containing a known amount of **6** ranging between 0.08 and 0.1 mmol in 5 mL of $C_6D_6$ in a 200-mL Schlenk tube was connected to a mercury manometer and a 1-L reservoir. The tube was cooled to −78 °C and the whole system (total volume 1.25 L) evacuated before returning the tube to the reaction temperature. Then propene was introduced and the pressure recorded (usually around 150 torr of propene was added). The consumption of propene was followed for up to ca. 5000 min with a total pressure change of 3–8 torr, depending on temperature. The reaction temperatures used were −20 °C and room temperature. After terminating the reaction, $^1$H and $^{13}$C NMR analysis of the now red solution showed the presence of **7**, free $NEt_3$, and propene. A white insoluble product was formed during the reaction and it was isolated by removal of the solvent under vacuum. The analyses of the solid from the two runs gave C, 17.46 (RT) and 23.81, 24.03 (−20 °C); H, 4.61 (RT) and 5.28, 5.56 (−20 °C); and N, 0.02 (RT) (calculated for propene: C, 85.63; H, 14.37).

An independent experiment was carried out under conditions such that the reaction could be monitored by $^1$H NMR. A sample of **6** in $C_6D_6$ was placed in an NMR tube with propene at 1 atm pressure. Spectra were then obtained as a function of time with the propene atmosphere being replenished once after the reaction rate approached zero.

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# ($\eta^1$-Acyl)titanium Complexes Prepared by the Carbonylation of 1-Oxa-5-titanacyclopentanes

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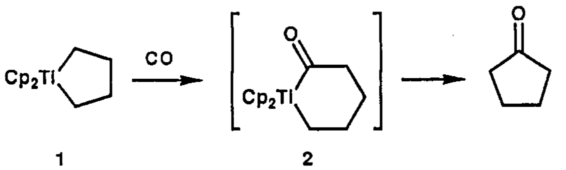
Carbonylation of 1-oxa-5-titanacyclopentanes $Cp^*_2\overline{TiOCH(R)CH_2C}H_2$ (**3**: **a**, R = $CH_3$; **b**, R = $CH_2CH_3$; **c**, R = $CHMe_2$; Cp* = pentamethylcyclopentadienyl) in toluene at room temperature under atmospheric pressure of CO afforded $Cp^*_2\overline{TiOCH(R)CH_2CH_2C}O$ (**4**: **a**, R = $CH_3$ (81%); **b**, R = $CH_2CH_3$ (77%); **c**, R = $CHMe_2$ (81%)) whose structures have been characterized by spectral data and X-ray analysis. X-ray structure determination of **4c** revealed that it has a novel $\eta^1$-acyltitanium structure [space group $P2_1/n$ with cell constants $a$ = 17.874 (4) Å, $b$ = 16.170 (4) Å, $c$ = 8.580 (1) Å, and $\beta$ = 92.69 (1)°, $V$ = 2482.4 (9) Å$^3$ (2544 reflections, $R$ = 0.060)]. Reaction of **3** with isocyanide gave the iminoacyl complexes $Cp^*_2\overline{TiOCH(R)CH_2CH_2C}(NCMe_3)$ (**6**: **a**, R = $CH_3$; **b**, R = $CH_2CH_3$, **c**, R = $CHMe_2$). The molecular structure of **3c** [space group $P2_1/a$ with cell constants $a$ = 18.529 (3) Å, $b$ = 16.308 (2) Å, $c$ = 8.547 (1) Å, and $\beta$ = 111.24 (1)°, $V$ = 2407.3 (6) Å$^3$ (1949 reflections, $R$ = 0.051)] has also been determined by X-ray crystallography.

## Introduction

Carbonylation of five-membered metallacycles giving cyclopentanone derivatives has attracted much attention as a promising way for building up five-membered carbocycles.[1-3] Titanacyclohexanone **2** has been postulated as an important intermediate in the carbonylation of titanacyclopentane **1**. Experimental evidence on the mechanism of carbonylation, however, has been limited due to the thermal and/or kinetic lability of the intermediate such



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