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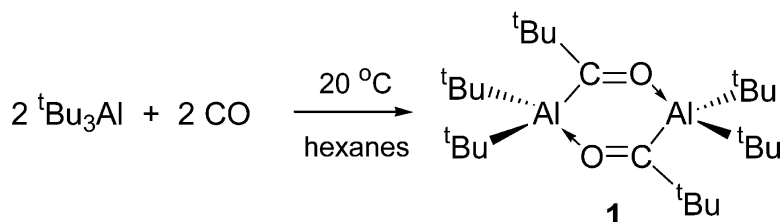
Remarkable Room-Temperature Insertion of Carbon Monoxide into an Aluminum–Carbon Bond of Tri-*tert*-butylaluminum

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Remarkable Room-Temperature Insertion of Carbon Monoxide into an Aluminum−Carbon Bond of Tri-*tert*-butylaluminum

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Aluminum alkyls are highly reactive with a variety of simple molecules including oxygen, water, carbon dioxide, hydrogen, and alkenes.[1,2] Investigations of this reactivity have led to the development of commercially important aluminum alkyl catalysts and cocatalysts for the polymerization of alkenes,[3] dienes,[4] and epoxides,[5] as well as for the production of linear terminal alkenes and alcohols.[1,2,6] Surprisingly, carbon monoxide is noticeably absent from the list of simple molecules that participate in the extensive chemistry of aluminum alkyls.[1,2] This is even more surprising when one considers that some common main group organometallics such as lithium alkyls,[7] Grignard reagents,[8] and alkylboranes[9] undergo CO insertion reactions.

The lack of reactivity of aluminum alkyls with carbon monoxide has been assumed to be the inability of aluminum, as well as other main group metals, for M → CO π* back-bonding. However, recent work by Strauss shows that carbon monoxide can bind effectively to Lewis acidic transition metal ions in the absence of back-bonding.[10] To do so requires that Lewis bases that would otherwise compete with CO for metal coordination sites, including anions, be excluded from the reaction system. With this knowledge, nontraditional homoleptic carbonyl complexes have now been reported for Cu^+, Ag^+, Au^+, Hg^{2+}, Pd^{2+}, and Pt^{2+}. Main group metal ions and complexes should be no exception,[11] and even decamethylcalcocene has been shown to bind CO under pressure.[12]

Some group 13 elements and their complexes have been demonstrated to bind carbon monoxide in both the presence and the absence of π-bonding. Borane carbonyl has been known since 1937,[13] and complexes such as $(X_2B)_3BCO$ (X = Cl, F),[14] $(CF_3)_3$-BCO,[15] B_4X_6CO (X = F, Cl, Br, I),[16] and $B_4(CO)_2$ [17] have since been reported. Matrix isolation studies demonstrate that Al, Ga, and In atoms form carbonyl moieties at 20 K.[18] Similarly, Sanchez, Arrington, and Arrington reported that monomeric trimethylaluminum forms the carbonyl complex Me_3AlCO in an argon matrix at 15−35 K.[19] No room-stable carbonyl complexes of aluminum have been reported, nor have any reactions of carbon monoxide with aluminum alkyls.

The results of Sanchez, Arrington, and Arrington[19] deserve particular mention. In their study, dimeric trimethylaluminum was heated to 300 °C, which subsequently led to a 200:1 ratio of monomer to dimer in the deposited matrix. Increased monomer concentration resulted in increased formation of Me_3AlCO at 15−35 K. The IR signature for this complex was lost upon warming. This can be interpreted in two ways: carbonyl dissociation followed by dimerization of Me_3Al, or CO insertion to give an acyl complex. The authors did not comment on the fate of the complex upon warming other than to state that the spectroscopic signatures for Me_3AlCO were lost.

On the basis of the results of Sanchez, Arrington, and Arrington, we hypothesized that an aluminum alkyl that is a monomer at room temperature might similarly bind carbon monoxide and, possibly, result in CO insertion. We set out to test this hypothesis by reaction

of carbon monoxide with $^tBu_3Al$. Unlike most aluminum alkyls for which dimerization is strongly favored, $^tBu_3Al$ is a monomer at room temperature.[20] Furthermore, $^tBu_3Al$ readily inserts ethylene to give trineohexylaluminum under much milder conditions (20 °C, 60 atm) than those needed for insertion of ethylene into dimeric aluminum alkyls such as Me_3Al (110−120 °C, 150 atm) and Et_3-Al (100−120 °C, 50−100 atm).[21] For dimeric aluminum alkyls, ethylene insertion rates are half-order in aluminum alkyl concentration, indicating that dissociation to monomer is required prior to ethylene insertion, again suggesting that monomeric aluminum alkyls would be most likely to insert carbon monoxide.

Addition of carbon monoxide to a flask containing a solution of $^tBu_3Al$ in hexanes quickly resulted in the colorless solution becoming bright yellow (eq 1).
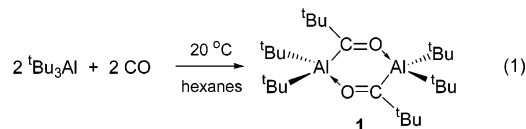
Stirring the reaction solution at room temperature and atmospheric pressure overnight gave yellow crystalline [$^tBu_2AlC(O)^tBu$]$_2$ (**1**) in 62% yield.[22] Analytical samples of **1** were obtained by recrystallization from THF.[23] The product was formulated as a bridging *tert*-butylacyl dimer based on NMR spectroscopy, IR spectroscopy, and elemental analysis. The ^1H NMR spectrum of a C_6D_6 solution of **1** exhibits singlet ^tBu resonances at 1.12 and 0.97 ppm with relative intensities of 2:1. The $^{13}C\{^1H\}$ NMR spectrum of **1** similarly shows singlet methyl resonances at 31.04 and 24.96 ppm in an approximate 2:1 ratio for aluminum-bound ^tBu and *tert*-butylacyl groups, as well as a singlet at 51.64 ppm and a quadrupolar-broadened resonance at 15.44 ppm for the quaternary ^tBu carbons. A very low-intensity resonance was observed at 327 ppm assigned to the carbonyl carbon of the acyl.

The infrared spectrum of **1** does not exhibit a band in the range anticipated for either a terminal carbonyl or a terminal acyl moiety. There is, however, a band at 1527 cm^{-1} assigned to ν(CO) for a bridging acyl.[24]

To verify the IR and NMR assignments and to confirm that CO had indeed been incorporated into the product, $^tBu_3Al$ was exposed to 99% isotopically enriched ^{13}CO to give [$^tBu_2Al^{13}C(O)^tBu$]$_2$ (**1-^{13}C**). The IR band at 1527 cm^{-1} assigned to ν(^{12}CO) for **1** was shifted to 1493 cm^{-1} for **1-^{13}C** as predicted for ν(^{13}CO). The ^1H and ^{13}C NMR data are even more conclusive as to CO insertion. The ^1H NMR spectrum for **1-^{13}C** exhibits a singlet ^tBu resonance at 1.12 ppm for the terminal ^tBu groups on aluminum, and the acyl ^tBu resonance at 0.97 ppm is split into a doublet with $^3J_{CH}$ of 4.4 Hz. This coupling compares favorably with that in $Et_2{}^{13}C$=O ($^3J_{CH}$ = 4.7 Hz) and $^iPr_2{}^{13}C$=O ($^3J_{CH}$ = 5.1 Hz).[25] The $^{13}C\{^1H\}$ NMR spectrum exhibits doublet resonances at 51.6 ppm ($^1J_{CC}$ = 19.9 Hz) and 24.9 ppm ($^3J_{CC}$ = 2.5 Hz) assigned to the quaternary and
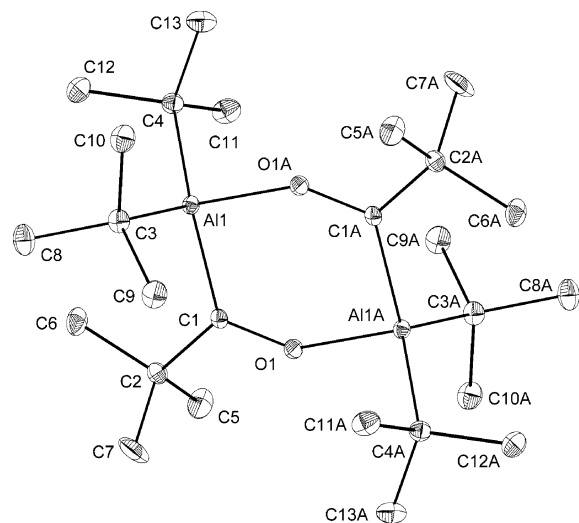
Figure 1. ORTEP drawing of [^{t}Bu$_2$AlC(O)^{t}Bu]$_2$ (**1**). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

methyl carbons, respectively, of the bridging *tert*-butylacyl moiety. The observation of $^{13}C-^{13}C$ coupling substantiates insertion of the labeled ^{13}CO into an Al−C bond. In addition, the isotopically enriched acyl carbon resonance is easily observed as an intense singlet at 327.1 ppm.

The molecular structure of **1** was further confirmed by X-ray crystallography at 120 K as shown in Figure 1. Two ^{t}Bu$_2$AlC(O)^{t}Bu moieties are related by a crystallographic inversion center and connected by μ_2-η^2-*tert*-butylacyls to form an Al$_2$C$_2$O$_2$ six-membered ring. Aluminum atoms are approximately tetrahedral. The aluminum−oxygen distance of 1.866(2) Å and the carbon−oxygen distance of 1.252(3) Å are in the ranges reported for ketones coordinated to four-coordinate aluminum atoms.[26]

These data leave little doubt as to the identity of the product and the fact that it was formed by CO insertion. Control experiments showed that common trace impurities in commercially available CO were not the cause for the observed reactivity. Reaction products of ^{t}Bu$_3$Al with H$_2$O,[27] O$_2$,[28] and CO$_2$ [21a] have been previously characterized.

As a check on the importance of the three-coordinate nature of aluminum for effecting this insertion reaction, ^{t}Bu$_3$Al was treated with THF or diethyl ether prior to exposure to CO to give four-coordinate adducts ^{t}Bu$_3$Al·THF or ^{t}Bu$_3$Al·OEt$_2$. These adducts do not react with CO at atmospheric pressure and room temperature. Similarly, dimeric aluminum alkyls (R$_3$Al, R = Me, Et, ^{i}Bu) did not react with CO under these reaction conditions. This is consistent with known data, including results of Tritto and co-workers who demonstrated that tridecylaluminum does not react with CO at atmospheric pressure and room temperature over a period of two weeks.[29]

Additional preliminary results indicate that factors other than the coordination number at aluminum are important for effecting CO insertion into an Al−C bond. Further results of our studies on reactions of CO with group 13 compounds will be reported.

Supporting Information Available: Crystallographic data in CIF format and experimental section for the preparation of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Short reaction times (e.g., 5 min) yield a mixture of **1** and a second product, **2**. The second product can be removed by recrystallization of crude **1** from THF or avoided altogether by using longer reaction times. The formation and chemistry of **2** is still under investigation.

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