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Alkylaluminum-Induced Diamide Transfer from Group 6 Imido Diamido Complexes

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*Summary: Reaction of $AlMe_3$ with the imido compounds $Mo(NPh)(o\text{-}(SiMe_3N)_2C_6H_4)(CH_2)_4$ (**1**) and $Mo(NPh)(o\text{-}(SiMe_3N)_2C_6H_4)L$ (**2**; L = diphenylacetylene) results in the transfer of the diamide ligand to the Al, giving the unusual arene complexes **3** and **4**.*

Neutral aluminum complexes of the form AlX_3 (X = halide, alkyl, etc.) have been extensively utilized in organic synthesis as Lewis acid reagents and as catalysts and cocatalysts in organotransition-metal-mediated polymerizations or oligomerizations.[1] Examples of this include Ziegler−Natta and metallocene-based polymerization systems, wherein a transition-metal complex is treated with an aluminum reagent, e.g. Et_2AlCl_2 or MAO, in the presence of olefin at high pressure. In these cases, the aluminum reagent acts as an alkylating agent; however, the exact nature of the catalytic species that arise from the interaction of the transition metal with the aluminum reagent is still the subject of some debate.[2]

In our laboratories we have had success in synthesizing high-oxidation-state imido complexes of the form $M(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)X_2$ (M = Mo, W)[3] incorporating the o-$(Me_3Si)_2$-pda (pda = phenylenediamide) ligand. We have shown that this ligand stabilizes the metal center via π donation of the diamide lone pair electrons, and we have been able to synthesize complexes incorporating various functional groups, e.g. metallacycles,[4] alkyls, olefins,[5] and alkynes, with both Mo and W.

In an attempt to produce a catalyst that selectively generates 1-hexene from propylene, Exxon[6] revisited a catalytic system first developed by Lawson[7] and Menapace[8,9] involving an aniline/WCl_6/Al mixture with a low Al to W ratio (5:1). Their observation that metallacyclopentanes were formed during this catalysis inspired us to examine the reaction of our metallacyclopentane complexes with aluminum reagents to investigate the catalytic activity of the resultant products.

Treatment of an orange solution of $Mo(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)(CH_2)_4$ (**1**) in toluene with 1 equiv of trimethylaluminum (TMA) results in a green solution after 15 min. Concentration of the solution and subsequent

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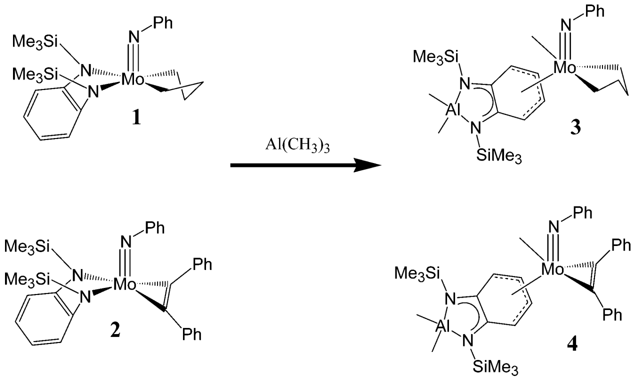
Scheme 1



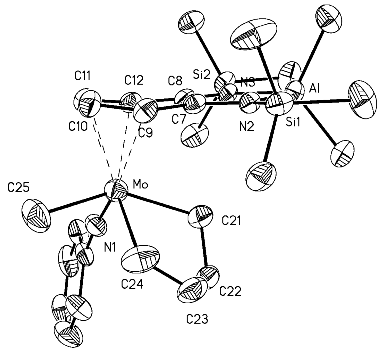


Figure 1. Thermal ellipsoid plot of **3** (40% ellipsoids). The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Mo−N(1) = 1.725(3), C(7)−C(8) = 1.469(4), C(8)−C(9) = 1.421(4), C(9)−C(10) = 1.408(4), C(10)−C(11) = 1.384(5), C(11)−C(12) = 1.400(4), C(12)−C(7) = 1.418(4), N(2)−C(8) = 1.335(4), N(3)−C(7) = 1.346(4), Al−N(2) = 1.925(2), Al−N(3) = 1.926(2).

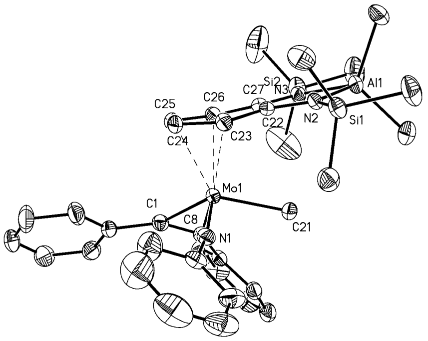


Figure 2. Thermal ellipsoid plot of **4** (40% ellipsoids). Hydrogens have been omitted for clarity. Selected bond lengths (Å): Mo(1)−N(1) = 1.752(2), C(22)−C(23) = 1.403(4), C(23)−C(24) = 1.405(4), C(24)−C(25) = 1.398(4), C(25)- - - C(26) = 1.404(4), C(26)−C(27) = 1.416(4), C(22)−C(27) = 1.478(4), C(22)−N(3) = 1.349(3), C(27)−N(2) = 1.339(3), Al(1)−N(3) = 1.923(2), Al(1)−N(2) = 1.926(2).

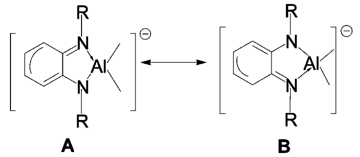
crystallization from pentane (at −78 °C) results in the isolation of green crystals of **3**, a metallacyclopentane methyl complex (Scheme 1). A similar reaction occurs when an orange solution of the diphenylacetylene complex **2** is treated with 1 equiv of TMA. The resultant yellow diphenylacetylene methyl complex precipitates from pentane after stirring for 24 h.

This transformation is similar to the reactions between alkylaluminum reagents and lanthanide or early-transition-metal amides which produce aluminate[10] or hydride[11] complexes. The reaction is driven by the formation of the Al−N bond of the aluminum amide complex that is also formed in the reaction. There are apparently no examples of such an exchange reaction involving an alkylaluminum reagent and a diamide ligand bound to a transition metal or lanthanide. As shown in Scheme 1, the $R_2Al(o\text{-}(Me_3SiN)_2\text{-pda})$ anion that is formed in the reaction is trapped by coordination of its arene ring to the molybdenum center.

The ^{1}H NMR spectra of **3** and **4** reveal the presence of highly shielded aromatic peaks (4.7−5.5 ppm), suggesting π coordination of the aromatic ring to the Mo center. The metallacyclopentane ring protons in **3** appear as multiplets (1.8−3.2 ppm). Three different methyl groups and two signals for the protons of the $SiMe_3$ groups are also observed, while the phenylimido protons appear as a multiplet at 6−8 ppm. The proton NMR spectrum of **4** is also consistent with the presence of a π-coordinated arene ring and a Mo methyl group. These structures were confirmed by single-crystal X-ray diffraction studies.

The thermal ellipsoid plots of **3** and **4** are presented in Figures 1 and 2. A distorted square pyramid with the *o*-pda ring occupying the apical position best describes the coordination geometry about molybdenum. The aluminum−nitrogen bond lengths are typical of Al−N single bonds (1.925 Å). The pda phenyl ring binds to the metal in an η^4-fashion in both complexes, but this bonding is not symmetrical. The metal−carbon bond distances Mo−C10 (**3**) and Mo−C24 (**4**) are significantly shorter (2.334 and 2.348 Å, respectively), than the adjacent metal−carbon bonds Mo−C9 and Mo−C11 (2.414 and 2.464 Å, respectively) in **3** and Mo−C23 and Mo−C25 (2.463 and 2.392 Å) in **4**. The fourth metal−carbon bond Mo−C12 (**3**) and Mo−C26 (**4**) of this butadienyl fragment is significantly longer (2.605 and 2.549 Å, respectively). The carbon−nitrogen bond lengths (average 1.341 and 1.344 Å for **3** and **4**, respectively) are slightly shorter than typical for diamide (1.38−1.42 Å)[12] complexes but longer than for diimine complexes (1.28 Å).[13] Also, the carbon−carbon bonds of the benzenoid framework are characterized by long $C_\alpha-C_{\alpha'}$ bonds (1.469 and 1.478 Å).

These data suggest that contributions from the two resonance forms **A** and **B** describe the interaction between the arene fragment and the Mo center. These resonance structures account for the shortened C−N bonds (relative to a diamide structure) and the relatively long $C_\alpha-C_{\alpha'}$ bonds that are consistent with a single bond between two sp^2 carbon atoms.



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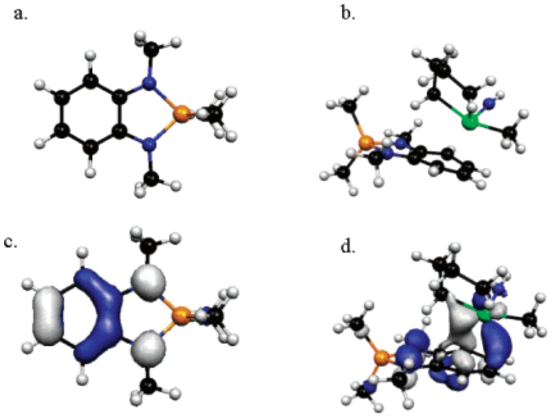

Figure 3. Optimized B3LYP structures for the model complexes $Me_2Al(o\text{-}(Me_3N)_2\text{-pda})^-$ (**5**) and $(CH_2)_4Mo(CH_3)(NH)(o\text{-}(Me_3N)_2C_6H_4)Al(CH_3)_2$ (**6**) and their molecular orbitals.

DFT calculations[14] were performed on the model compounds $[Me_2Al(o\text{-}(Me_3N)_2\text{-pda})]^-$ (**5**) and $(CH_2)_4Mo(CH_3)(NH)(o\text{-}(Me_3N)_2C_6H_4)Al(CH_3)_2$ (**6**) to understand the structure and bonding in these new complexes. Optimized structures for these models are depicted in Figure 3 along with the molecular orbital plot of the HOMO (**3c**) of this anion. The benzenoid portion of the HOMO is of π symmetry, which is ideal for interaction with the empty metal dπ orbitals. The metal center being asymmetric binds strongly with three atoms in **6**, while the fourth carbon is less strongly bound, due to the trans influence of the imido ligand, as is observed in the structures of **3** and **4** (Figure 3d).

In summary, we have demonstrated the first example of a diamide transfer reaction between trimethylaluminum and an early transition metal. This transformation involves the formation of a very unusual aluminum anion that stabilizes the molybdenum via π-donor interactions. Transfer of carbon to aluminum is known to be an important chain transfer process in aluminum-activated α-olefin polymerization reactions. The similar transfer of other ligands to Al, such as diamides, has not been investigated.[15] These results show the N−Al transfer is possible in early-transition-metal complexes and suggests that such processes may be possible in diamide-containing polymerization catalysis.[16] Preliminary results show that **3** catalyzes the dimerization of ethylene, giving 1-butene at room temperature and 1 atm of ethylene pressure. We are currently investing the utility of these complexes as olefin dimerization catalysts and their relevance to group 4 non-metallocene[15] polymerization systems.

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Supporting Information Available: Full details for experimental procedures and crystallographic data for compounds **3** and **4**, including tables of crystal data and data collection parameters, atomic coordinates, anisotropic displacement parameters, and all bond lengths and bond angles, and full details of all methods used for molecular orbital calculations in addition to tables of atomic coordinates for **5** and **6**; crystallographic data for **3** and **4** are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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