Synthesis and Molecular Structure of $AlMe(PhNNNPh)_2(3,5\text{-}Me_2py)$: The First Observation of the Trans Influence in an Aluminum Compound

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Summary: Reaction of trimethylaluminum with 1,3-diphenyltriazene in the presence of 3,5-dimethylpyridine affords the crystalline product $AlMe(PhNNNPh)_2(3,5\text{-}Me_2py)$, in which the triazenides act as chelating ligands around a distorted octahedral aluminum center. The presence of a long Al-N bond [2.155 (2) Å] trans to the methyl group is explained by the strong trans influence of the latter ligand. The compound crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions a = 9.631 (3) Å, b = 17.235 (6) Å, c = 18.026 (8) Å, β = 96.16 (3)°, Z = 4, observed data = 3212, R = 0.0421, and R_w = 0.0517.

Recent work in our laboratory has been concerned with understanding the relative importance of steric and electronic effects in determining the structure and reactivity of alkylaluminum compounds.[1,2] As part of this study, we have isolated the tetranuclear compound $\{[N(CH_2CH_2O)_3]Al_2(CH_3)_3\}_2$, which consists of two six-coordinate and two four-coordinate aluminum atoms and contains the first structurally characterized six-coordinate aluminum alkyl unit.[3] We now report the synthesis and characterization of the first monomeric octahedral aluminum alkyl.

The reaction of $AlMe_3$ with PhNNN(H)Ph [PhNNN(H)Ph = 1,3-diphenyltriazene] leads to a single product, $Al(PhNNNPh)_3$, in addition to the evolution of methane, even when a large excess of $AlMe_3$ is employed.[4] If, however, the reaction is carried out in the presence of a strong Lewis base, such as 3,5-dimethylpyridine, the less highly substituted compound $AlMe(PhNNNPh)_2(3,5\text{-}Me_2py)$ (1) can be isolated.[5] The IR spectrum[6] shows bands at 1320 and 1295 cm^{-1}, which are characteristic of chelating triazenide groups.[4] The chelating coordination mode has been confirmed by X-ray crystallography.[7]

The molecular structure of 1 is shown in Figure 1. The structure consists of discrete monomeric units with the aluminum atoms in a distorted octahedral configuration [N(1)-Al-N(7) = 159.2 (1)°, N(3)-Al-N(4) = 147.3 (1)°, N(6)-Al-C(32) = 169.3 (1)°]. The methyl and $3,5\text{-}Me_2py$ ligands are mutually cis, and the two triazenides act as bidentate chelating ligands. The observation of two distinct ^1H NMR resonances for the meta protons of the triazenide phenyl groups,[6] in a ratio of 3:1, is consistent with the retention of the cis isomer in solution. The Al-C(32) distance [1.999 (3) Å] is within experimental error of the $Al\text{-}CH_3$ distance [1.99 (1) Å] reported previously in the octahedral aluminum alkyl $\{[N(CH_2CH_2O)_3]Al_2Me_3\}_2$.[3] While the Al-N distances of the nitrogen cis to the methyl group [2.006 (2)-2.051 (2) Å] are within the range observed for amine adducts of $AlMe_3$ (1.88-2.09 Å),[8] the Al-N distance for the triazenide nitrogen trans to the methyl group is long, 2.155 (2) Å. The only comparable Al-N distances are for axial substituents in trigonal-bipyramidal aluminum compounds [2.135 (2)-2.193 (4) Å].[9] The lengthening in the present compound is undoubtably due to the large trans influence of the methyl group.[10] Although it is not surprising that a trans influence should be observed in group III compounds, this is, we believe, the first well-defined example to be reported for a non-transition-metal compound.

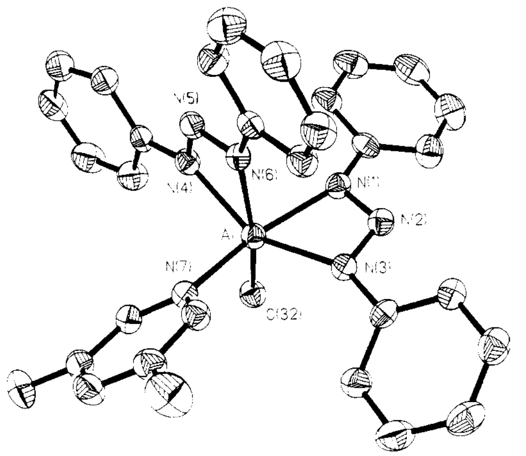

Figure 1. Molecular structure of 1. Thermal ellipsoids show 50% probability levels. Hydrogens have been omitted for clarity.

Despite the long Al-N(6) bond, no significant perturbations are observed within either triazenide ligand. The similarity between the N-N distances [1.307 (3)-1.326 (3) Å] implies a delocalization of the π-electrons in the N_3 portion of the ligand. The inclusion of the phenyl rings in the π-delocalization is suggested by the short N-C distances [$N\text{-}C_{av}$ = 1.416 (3) Å] which are significantly

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(1) (a) Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1988**, 3047. (b) Wierda, D. A.; Barron, A. R. *Polyhedron* **1989**, *8*, 831.

(2) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, 7, 2543.

(3) Healy, M. D.; Barron, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 398.

(4) Leman, J. T.; Barron, A. R.; Ziller, J. W.; Kren, R. M. *Polyhedron*, in press.

(5) PhNNN(H)Ph (1.97 g, 10 mmol) was dissolved in toluene (25 mL) and the mixture added to a toluene (50 mL) solution of $AlMe_3$ (7.5 mL, 2 M solution in hexane, 15 mmol) at 0 °C. Immediately after the addition was complete, $3,5\text{-}Me_2py$ (1.1 mL, 10 mmol) was added and the reaction allowed to warm to room temperature and stirred for 12 h. The solvent was removed resulting in a yellow powder which was recrystallized from toluene/pentane (2:1, v/v): yield, crude, ca. 30%, after recrystallization, 0.32 g, 12%; mp 199-200 °C.

(6) ^1H NMR (C_7D_8, δ): 8.32 (2 H, s, *o*-H, $3,5\text{-}Me_2py$), 7.62 (6 H, d, J(H-H) = 7.8 Hz, *o*-H, *cis*-Ph), 7.54 (2H, d, J(H-H) = 7.8 Hz, *o*-H, *trans*-Ph), 7.14 (8 H, dd, J(H-H) = 7.6 Hz, *m*-H, Ph), 7.88 (4 H, t, J(H-H) = 7.6 Hz, *p*-H, Ph), 6.42 (1 H, s, *p*-H, $3,5\text{-}Me_2py$), 1.52 (6 H, s, CH_3, $3,5\text{-}Me_2py$), 0.14 (3 H, s, $Al\text{-}CH_3$). IR (Nujol, NaCl, cm^{-1}): 1590 (s), 1480 (s), 1320 (m), 1295 (s), 1275 (s), 1230 (s), 1150 (m), 1070 (m), 1015 (m), 900 (w), 865 (w), 790 (w), 760 (m), 690 (m), 660 (m).

(7) Crystal data for $AlMe(PhNNNPh)_2(3,5\text{-}Me_2py)$: monoclinic, $P2_1/c$, a = 9.631 (3) Å, b = 17.235 (6) Å, c = 18.026 (8) Å, β = 96.16 (3)°, V = 2975 (2) Å^3, Z = 4, D(calcd) = 1.209 g cm^{-3}, λ(Mo K_α) = 0.71073 Å (graphite monochromator), T = −80 °C. A Nicolet R3m/v diffractometer, equipped with a LT-1 low-temperature device, was used to collect 4356 reflections ($4° < 2\theta < 45°$) on an orange crystal (0.41 × 0.25 × 0.30 mm). Of these 3912 were independent, R_{int} = 1.67% and 3212 observed [$F_o > 4\sigma(F_o)$]. A semiempirical absorption correction based on Ψ scans and Lorentz and polarization corrections were applied to the data. The Al atom was located by direct methods. Standard difference map techniques were used to find the remaining non-hydrogen atoms. All Al, N, O, and C atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions [$U_{iso}(H) = 1.2U_{iso}(C)$; $d_{C\text{-}H}$ = 0.96 Å] for refinement. R = 0.0421, R_w = 0.0517, GOF = 1.88, and final residual = 0.24 e Å^{-3}. All computations used SHELXTL-PLUS: Sheldrick, G., Nicolet Corp., Madison, WI, 1987.

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shorter than the N–C single bond length of 1.472 Å.[11] It should be noted, however, that while the phenyl groups on one triazenide ligand [N(4)–N(6)] are almost coplanar with the N_3 plane, the phenyl groups on the other triazenide [N(1)–N(3)] are twisted (22° and 26°) with respect to the N_3 plane. The lack of significant variation in the N–C bond distances between the triazenide ligands, in spite of the difference in orientation of the phenyl rings, suggests that any delocalization of the N_3 π-system with the phenyl rings is relatively insensitive to torsion about the N–C bonds.

Compound 1 represents the first monomeric six-coordinate organometallic aluminum compound to be characterized structurally as well as the first observation of the trans influence in an aluminum compound.

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Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, and bond distances and angles (5 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Oxidative and Thermal Isomerization of Phosphido-Bridged Molybdenum Dicobalt Clusters: X-ray Crystal Structures of the Complexes $[MoCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ and $[NEt_4][MoCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$

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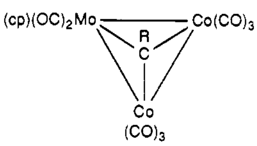
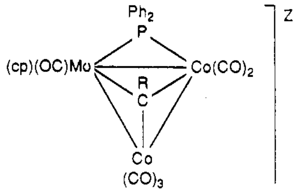
Summary: The anion 2^- undergoes two reversible one-electron oxidations, to 2 and 2^+, and is protonated to give 2-H which equilibrates with 3-H via thermal migration of the μ-PR_2 ligand; deprotonation of 2-H $\rightleftharpoons$ 3-H gives 3^- which is converted to 2 via a novel oxidatively induced μ-PR_2 migration reaction.

Treatment of metal carbonyl complexes with secondary phosphines can provide an efficient route for the synthesis of new phosphido-bridged derivatives.[1-3] The heterotrimetallic complexes $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ and $[WCo_2(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me) with PPh_2H give well-defined complexes $[WFe_2(\mu\text{-}H)(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_7(\eta\text{-}C_5H_5)]$ and $[WCo_2(\mu\text{-}H)(\mu_3\text{-}CR)(\mu\text{-}PPh_2)(CO)_6(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me), in which the μ-PPh_2 ligand bridges either the heteronuclear W–Fe or the homonuclear Co–Co bond, respectively.[4] Herein we report reactions on the $MoCo_2$ complex 1 which show that μ-PPh_2 ligands may undergo novel redox-induced dynamic behaviour leading to facile interconversion of isomers in which the μ-PPh_2 ligand bridges either the homonuclear Co–Co or the heteronuclear Mo–Co bond.

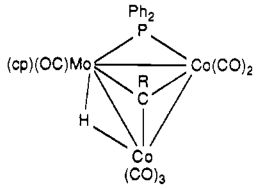
Treatment of 1 with 1 equiv of $LiPPh_2$ in tetrahydrofuran gives a highly reactive anion 2^- which is readily oxidised by air or $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ affording the stable 47 cluster valence electron radical 2.[5] The cyclic voltammogram[6] (CV) of 2 shows the expected reversible one-electron reduction to 2^- ($E° = -0.55$ V) and also reveals a reversible one-electron oxidation to 2^+ ($E° = 0.39$ V). The structure of the radical 2 was established by a single-crystal X-ray diffraction study[7] which confirms that the μ-PPh_2 ligand bridges a Mo–Co bond (Figure 1). The reversibility of the CV waves described above implies that no gross structural rearrangement takes place on oxidation or reduction.



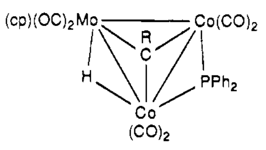
(1)



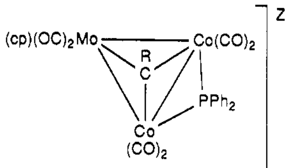
$(2)^z$ (Z = +1, 0, −1)



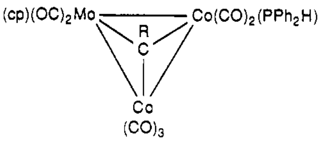
(2)-H



(3)-H



$(3)^z$ (Z = +1, 0, −1)



(4)

R = C_6H_4Me-4, cp = (η-C_5H_5)

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[5] Selected spectroscopic data (^{1}H NMR in CD_2Cl_2, and $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR in CD_2Cl_2–CH_2Cl_2 unless otherwise noted; coupling constants in Hz). Compound 2^-: IR (ν_{CO}(max), CH_2Cl_2) 2003 s, 1944 vs, 1893 m, 1849 w, sh cm^{-1}; $^{31}P\{^1H\}$ δ 170.9 (MoCo(μ-P)) ppm. Compound 2: IR (ν_{CO}(max), CH_2Cl_2) 2055 s, 2002 vs, br, 1887 w, br cm^{-1}. Compound 2^+: IR (ν_{CO}(max), CH_2Cl_2) 2094 s, 2054 vs, 2004 vs, 1920 cm^{-1}. Compound 2-H: IR (ν_{CO}(max), CH_2Cl_2) 2054 s, 2020 vs, 1984 s, sh, 1880 w, br cm^{-1}; ^{1}H NMR δ −13.56 [d, 1 H, μ-H, J(PH) = 12]; $^{31}P\{^1H\}$ δ 196.4 ppm (MoCo(μ-P)); $^{13}C\{^1H\}$ δ 255.2 [d, μ-CR, J(PC) = 22], 228.8 [d, MoCO, J(PC) = 17]. Compound 3-H: IR (ν_{CO}(max), CH_2Cl_2) 2039 m, 2010 vs, 1982 s, 1860 w, br cm^{-1}; ^{1}H NMR δ −13.34 [d, 1 H, μ-H, J(PH) = 22]; $^{31}P\{^1H\}$ δ 229.5 ppm (br, Co_2(μ-P)); $^{13}C\{^1H\}$ δ 256.9 [d, μ-CR, J(PC) = 24], 238.1, 220.5 (2 × s, 2 × MoCO). Compound 3^-: IR, (ν_{CO}(max), CH_2Cl_2) 1989 s, 1950 vs, 1924 s, 1840 br, 1800 w, br cm^{-1}; $^{31}P\{^1H\}$ δ 178.2 ppm (Co_2(μ-P)); $^{13}C\{^1H\}$ δ 264.5 [d, μ-CR, J(PC) = 17]. Compound 3: IR (ν_{CO}(max), CH_2Cl_2) 2032 m, 1988 vs, 1956 m, 1923 w, br, and 1870 w, br cm^{-1}. Compound 4: IR (ν_{CO}(max), CH_2Cl_2) 2049 m, 2010 s, 2002 s, 1989 s, 1912 w, br cm^{-1}; $^{31}P\{^1H\}$, δ 38.7 ppm (br, PPh_2H); $^{13}C\{^1H\}$ δ 262.0 (μ-CR).

[6] Cyclic voltammetry was carried out at a platinum bead electrode in CH_2Cl_2 0.1 mol dm^{-3} in $[NBu^n_4][PF_6]$ as supporting electrolyte. Potentials are quoted vs the saturated calomel electrode; $E°$ for the oxidation of ferrocene, added as an internal standard, was 0.47 V under the experimental conditions used.