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Reactivity of 1-Aza-4-oxo-1,3-butadienes (α-Imino Ketones) toward Triorganoaluminum Reagents. 1. X-ray Crystal Structures of $[(AlMe_3)_2\{\sigma,\sigma\text{-N,O-}(MeN{=}C(Ph)C(Ph){=}O)\}]$, with a N,O-Bridge-Bonded α-Imino Ketone, and of $Me_2\overline{Al(\textit{t}\text{-}Bu)N{=}CHC(Me)_2O}AlMe_3$, a Carbonyl Alkylated Product Which Is O-Coordinated to $AlMe_3$

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Triorganoaluminum reacts with stoichiometric quantities of α-imino ketones in hexane to form the 2:1 complexes $[(AlMe_3)_2\{\sigma,\sigma\text{-N,O-}(R^1N{=}C(R^2)C(R^3){=}O)\}]$ (1) which depending on the substitution pattern of the α-imino ketone are stable and can be isolated. Crystals of **1a** are monoclinic with space group $C2/c$ and cell constants $a = 20.110$ (2) Å $b = 13.819$ (1) Å $c = 18.813$ (3) Å, $\beta = 115.18$ (1)°, and $Z = 8$. The structure was refined to a final $R = 0.046$ with 2699 observed reflections. The σ,σ-N,O-bridged coordinated α-imino ketone ligand has the Z configuration at the imine bond (C=N = 1.276 (3) Å). Furthermore, a central C(1)—C(8) distance of 1.520 (3) Å and a C(1)=O(1)/C(8)=N(1) torsion angle of 85.9(3)° are found. In most cases it was not possible to isolate the 2:1 $AlMe_3/\alpha$-imino ketone adducts because rapid subsequent conversion into the stable ketone-alkylated products $Me_2\overline{Al(R^1)N{=}C(R^2)C(R^3,Me)O}AlMe_3$ (2) occurred. An X-ray structure determination for $R^1 = t$-Bu, $R^2 = H$, and $R^3 = Me$ (**2c**) revealed its molecular structure with an $AlMe_3$ unit coordinated to the alkoxy oxygen atom. Crystals of **2c** are monoclinic with space group $P2_1/c$ and cell constants $a = 9.117$ (2) Å $b = 11.867$ (1) Å, $c = 17.324$ (5) Å, $\beta = 101.91$ (2)°, and $Z = 4$. The structure was refined to a final $R = 0.091$ with 1741 observed reflections. The conformations of the α-imino ketones in these and previously reported complexes, i.e., *trans*-$[PtCl_2(PEt_3)\{\sigma\text{-N-}(t\text{-}BuN{=}CHC(Me){=}O)\}]$, are compared. It is concluded that, contrary to the planar or almost planar conformations of the related 1,4-diaza-1,3-butadienes, the 1-aza-4-oxo-1,3-butadiene ligands do not possess a planar ligand skeleton neither as a free ligand nor in its monodentate or bridging complexes.

Introduction

In a recent paper we surveyed work on the activation of 2e- and 4e-bonded R-DAB (1,4-diaza-1,3-butadiene, RN=CHCH=NR) ligands by coordinated ZnR_2 and AlR_3 molecules.[2a] Depending on the nature of the substituents on both the R-DAB ligand skeleton and the metal center, selective C–C and/or C–N bond formation was observed.[2-4] It was established that in these reactions C–N bond formation was accompanied by the formation of stable organozinc or -aluminum radical complexes.[2] The initial complex formation between the organometallic reagent and substrate appeared to involve the R-DAB ligand in either one of its planar conformations; i.e., in the s-cis conformation for the ZnR_2 adduct and in the s-trans conformation for the AlR_3 adduct; see Figure 1. In a related study of substrates having a N=C—C=O skeleton a complex reactivity pattern was observed toward organozinc and -aluminum reagents. The type of product formed appeared to depend on the substitution pattern of the azaoxo butadiene as well as on the nature of the metal substrate.[5] A particulary striking difference between the 1,4-diaza- and 1-aza-4-oxo-1,3-butadiene ligands is the fact that the latter ligands have in the ground state the nonplanar gauche rather than the planar syn or planar anti conformation (vide infra). Accordingly, a different coordination behavior of these 1-aza-4-oxo-1,3-butadiene ligands toward ZnR_2 and AlR_3 may be anticipated. The structural features of recently characterized *trans*-$[PtCl_2(PEt_3)\{\sigma\text{-N-}(t\text{-}BuN{=}CHC(Me){=}O)\}]$ was already a first support for this expectation.[6] In the latter complex the 1-aza-4-oxo-1,3-butadiene ligand is monodentate N bonded with the N=C—C=O skeleton in the nonplanar gauche conformation.

It appeared extremely difficult to study the initial complex formation in the case of reactions of the 1-aza-4-oxo-1,3-butadienes with ZnR_2 or AlR_3 reagents because of the occurrence of fast transfer of the organo groups in the initial coordination complexes from either the Zn or the Al centers to the coordinated substrate. However, in $Me_2\overline{Al(t\text{-}Bu)N{=}CHC(Me)_2O}AlMe_3$, case we succeeded in the isolation and characterization by an X-ray structure determination of a stable coordination complex

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Table I. Crystal Data and Numerical Details of the Structure Analyses of [(AlMe$_3$)$_2${σ,σ-N,O-(MeN=C(Ph)C(Ph)=O)}] (1a) and [Me$_2$Al(*t*-Bu)N=CHC(Me)$_2$OAlMe$_3$] (2c)

	1a	2c
	(a) Crystal Data	
formula	$C_{21}H_{31}Al_2NO$	$C_{13}H_{31}Al_2NO$
M_r	367.45	271.36
cryst system	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$
a, Å	20.110 (2)	9.117 (2)
b, Å	13.819 (1)	11.867 (1)
c, Å	18.813 (3)	17.324 (5)
β, deg	115.18 (1)	101.91 (2)
V, Å^3	4731 (1)	1834.0 (7)
Z	8	4
D_{calcd}, g cm^{-3}	1.032	0.983
F(000), electrons	1584	600
cryst size, mm	0.2 × 0.2 × 0.5	0.15 × 0.25 × 1.30
μ, cm^{-1}	Cu Kα, 10.71	Mo Kα, 1.3
	(b) Data Collection	
temp, K	295	295
radiatn, Å	Cu Kα, 1.5418	Mo Kα, 0.71069
θ_{min}, θ_{max}, deg	2.6, 70	1.7, 22.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.45 + 0.15 \tan \theta$	$\Delta\omega = 0.70 + 0.35 \tan \theta$
cryst to detector dist, (mm)	173	173
hor and vert apert, mm	3, 4	3, 3
max time/refl, s	60	60
ref refl	334, 823	104, 002
data set	h, −24 → 24; k, 0 → 16; l, 0 → 22	h, −9 → 9; k, 0 → 12; l, 0 → 18
total refl	4709	2328
total unique refl	4386	2252
obsd data ($I > 2.5\sigma(I)$)	2699	1744
total X-ray exposure time, h	79	34
decay	linear to 50%	none
	(c) Refinement	
$R_F \equiv (\sum\|F_o - \|F_c\|\|)/\sum\|F_o\|$	0.046	0.091
$wR_F \equiv \{\sum w(F_o - \|F_c\|)^2/\sum wF_o^2\}^{1/2}$	0.051	0.096
w	$1/\sigma^2(F)$	1
no. of refined par	350	188
no. of refl	2699	1741
$(\Delta/\sigma)_{max}$	0.5	0.2
min and max residual density, eÅ^{-3}	−0.21, 0.22	−1.1, 0.3

[(AlMe$_3$)$_2${σ,σ-N,O-(MeN=C(Ph)C(Ph)=O)}] which is the first example of a complex containing a bridging aza–oxo ligand. The synthesis and structural features of this complex are reported here.

In the course of this study an other type of organoaluminum complex was also isolated and characterized by X-ray structure determination. This complex, Me$_2$Al(*t*-Bu)N=CHC(Me)$_2$OAlMe$_3$, is formed from the 2:1 coordination complex by subsequent transfer of one of the (Al)R groups to the oxo-carbon atom. It is therefore an example of one of the alkylation products formed in the reaction of Al$_2$Me$_6$ with 1-oxo-4-aza-1,3-butadiene substrates, and its structural features may be likewise important for understanding the activation of N=C—C=O skeletons by coordination to Al or Zn centers.

Experimental Section

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Solvents were carefully dried and distilled before use. The triorganoaluminum compounds are commercially available (Alfa) and were used without further purification. The α-imino ketones [R^{1}N=C(R^2)C(R^3)=O] with R^1 = Me, *i*-Prop and R^2 = R^3 = Ph as well as with R^1 = *t* Bu, R^2 = H, and R^3 = Me were prepared by published methods.[7,8] Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands. For all isolated compounds correct elemental analytical data were obtained.[9]

Synthesis of [(AlMe$_3$)$_2${σ,σ-N,O-(R^{1}N=C(Ph)C(Ph)=O)}] (1a, R^1 = Me, or 1b, R^1 = *i*-Prop). As an example the synthesis of [(AlMe$_3$)$_2${σ,σ-N,O-(MeN=C(Ph)C(Ph)=O)}] (1a) is described. A hexane solution of Al$_2$Me$_6$ (20 mmol, 1 M solution) was slowly added to a stirred solution of MeN=C(Ph)C(Ph)=O (8.88 mmol) in 100 mL of hexane at −60 °C which resulted in the immediate precipitation of a white solid. The whole mixture was warmed up to room temperature in 1 h, which provided a clear, yellow solution. After additional stirring for 1 h at 30 °C the clear reaction mixture was concentrated to 60 mL and then cooled to −20 °C. The new complex crystallized as small ochreous-yellow crystals, yield 2.56 g, (79%, calculated on the free α-imino ketone).

Synthesis of [Me$_2$Al(R^1)N=C(R^2)C(R^3,Me)OAlMe$_3$] (2a–c). The isolated coordination compounds described above (5 mmol) were dissolved in toluene (25 ml) and the solutions heated at 80 °C for 30 min. During this time the initially yellow solutions became colorless. Hexane was added (25 mL) and the solution then cooled to −30 °C. This resulted in the crystallization of the new complexes **2a** and **2b** as white needles, yield about 86%. Compound **2c** (R^1 = *t*-Bu, R^2 = H, and R^3 = Me) was synthesized by adding a hexane solution of Al$_2$Me$_6$ (20 mmol, 1 M solution) to a stirred solution of *t*-BuN=C(H)C(Me)=O (8.21 mmol) in 70 mL of hexane at 20 °C. After additional stirring for 1 h. the clear solution was concentrated to 30 mL and cooled to −20 °C. The new complex crystallized as small white crystals, yield 1.69 g (76%, calculated on the free α-imino ketone).

Structure Determination and Refinement. Crystal data and other numerical details of the structure determinations of [(AlMe$_3$)$_2${σ,σ-N,O-(MeN=C(Ph)C(Ph)=O)}] (1a) and [Me$_2$Al-

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A: chelate coordination B: monodentate coordination

Figure 1. A. Stable for R = Et below −50 °C. B. Stable for R = Et below −10 °C. Above these temperatures transfer of R to the heterobutadiene skeleton occurs (see ref 2 and 3 for A and ref 4 for B).

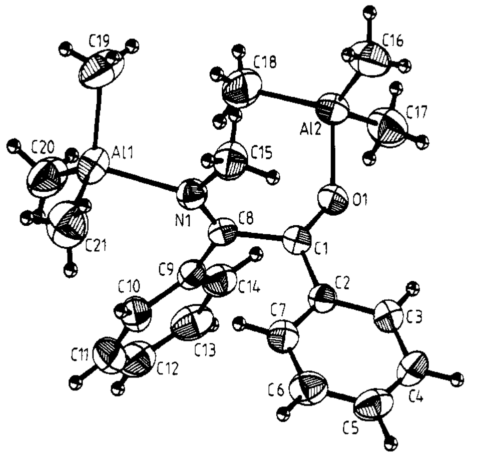


Figure 2. Ortep drawing of $[(AlMe_3)_2\{\sigma,\sigma\text{-N,O-}(MeN{=}C(Ph)C(Ph){=}O)\}]$ (**1a**) (40% level). The adopted numbering scheme is indicated.

(*t*-Bu)N=CHC(Me)$_2$OAlMe$_3$] (**2c**) are listed in Table I. Data sets were collected on an Enraf-Nonius CAD4F diffractometer for colorless crystals mounted in Lindemann glass capillaries. The data were corrected for Lorentz and polarization effects and the linear decay for **1a**. (The nature of the decay was not investigated; since both reference reflections indicated practically equivalent decay curves, it was considered to be unnecessary to add an additional time-dependent variance above the linearly upscaled counting statistics variance.)

Accurate values of the unit-cell parameters were derived by a least-squares procedure from the angular settings of 25 reflections. Systematic extinctions indicated $P2_1/c$ for **2c** and Cc or $C2/c$ for **1a**. The choice of the centrosymmetric alternative was confirmed by a satisfactory structure determination in $C2/c$.

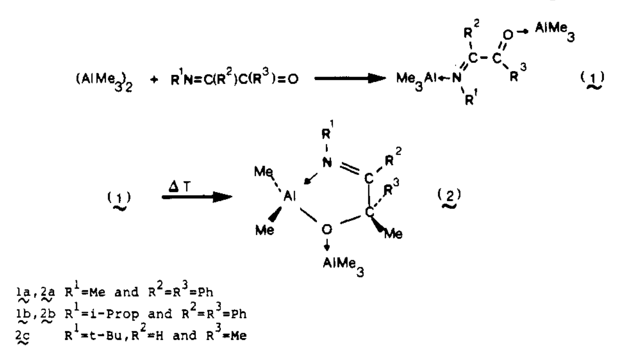
The structures were solved by direct methods (**1a**, SHELX 84;[10a] **2c**; MULTAN 80[10b]) and completed with Fourier methods. A full-matrix least-squares procedure minimizing $\sum w\Delta F^2$ was used for the refinement. The refined parameters included the scale factor, the positional parameters of the non-hydrogen atoms, and the positional and isotropic thermal parameters for the hydrogen atoms of structure **1a**. In the case of structure **2c** most hydrogen atoms were introduced at calculated positions (C–H = 1.08 Å) and refined in the riding mode on their carrier atoms with one overall isotropic temperature factor (U = 0.137 (4) Å^2), except for those attached to C(9), C(12), and C(19) where the methyl group hydrogen atoms could be located from the difference map. The methyl group C(13) was refined as a rigid group. Three reflections with a poor $\Delta F/\sigma$ ratio were excluded from the final cycles of the refinement of **2c**: refinement of **2c** with $w = 1$ led to the most satisfactory results.

Scattering factors for non-hydrogen atoms from Cromer and Mann[11] corrected for anomalous despersion[12] and for hydrogen from Stewart, Davidson, and Simpson[13] were used.

Calculations were carried out either on the in-house DG-Eclipse S/230 minicomputer using a locally adapted and extended version of the SHELX-76[14] package or on the CDC-Cyber 175 of the University of Utrecht with programs of the EUCLID package.[15]

Results and Discussion

The compounds $[(AlMe_3)_2\{\sigma,\sigma\text{-N,O-}(R^1N{=}C(R^2)(C(R^3){=}O)\}]$ (**1a,b**) with R^1, R^2, and R^3 as indicated in eq 1 have been obtained in almost quantitative yield from the reaction of Al$_2$Me$_6$ with the respective α-imino ketones in a 1:1 molar ratio in hexane. The reaction is complete within 30 min. The stability of **1a** and **1b** is surprising because normally Al$_2$Me$_6$ reacts rapidly with ketones and imines. For example, the (benzophenone)trimethylaluminum complex undergoes an irreversible first-order addition across the CO bond with a half-life of 48 min. at 25 °C.[16]



When (strongly) coordinating solvents are used like diethyl ether or THF or the reaction temperature is increased (vide infra), also in the case of the Al$_2$Me$_6$–α-imino ketone reactions subsequent product formation is observed. In coordinating solvents alkylation products or products originating from reduction reactions were obtained; see ref 17a. The coordination complexes **1a,b**, which have been isolated as yellow crystalline solids, have according to elemental analyses[9] 2:1 AlMe$_3$–α-imino ketone stoichiometry. Extensive ^{1}H and ^{13}C NMR experiments, which are discussed in ref. 17b confirmed the presence in these complexes of two AlMe$_3$ units coordinated to the respective N- and O-donor sites of the α-imino ketone ligand. Complexes **1** are soluble in dichloromethane and aromatic solvents but dissolve only slightly in hexane. These new trimethylaluminum coordination complexes are very air- and moisture-sensitive and decompose rapidly in air to give the free α-imino ketone ligands.

The compounds $\overline{Me_2Al(R^1)N{=}C(R^2)C(R^3,Me)O}AlMe_3$ (**2a–c**) with R^1, R^2, and R^3 as indicated in eq 1 have been obtained in almost quantitative yield from the reaction of Al$_2$Me$_6$ with the corresponding α-imino ketones in a 1:1 molar ratio. The reaction in hexane at 20 °C to compound **2c** is completed in 1 h. Also **1a,b** can be converted into compounds analogous to **2c** (**2a,b**), but then the solutions of **1a,b** in toluene have to be heated for 30 min at 90 °C.

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Table II. Positional Parameters and U_{eq} Values for the Non-Hydrogen Atoms and Their Estimated Standard Deviations for [(AlMe$_3$)$_2${σ,σ-N,O-(MeN=C(Ph)C(Ph)=O)}] (1a)

atom	*x/a*	*y*/b	*z*/c	U_{eq},[a] Å^2
Al(1)	0.36020 (4)	0.35665 (7)	0.23535 (5)	0.0642 (3)
Al(2)	0.16498 (5)	0.33074 (8)	0.37053 (5)	0.0653 (3)
O(1)	0.12053 (9)	0.3997 (2)	0.26850 (9)	0.0592 (5)
N(1)	0.2611 (1)	0.4064 (2)	0.2327 (1)	0.0521 (6)
C(1)	0.1330 (1)	0.4236 (2)	0.2119 (1)	0.0469 (8)
C(2)	0.0879 (1)	0.4931 (2)	0.1541 (1)	0.0467 (8)
C(3)	0.0219 (1)	0.5261 (2)	0.1537 (2)	0.0612 (8)
C(4)	−0.0188 (2)	0.5952 (3)	0.1013 (2)	0.0730 (10)
C(5)	0.0053 (2)	0.6332 (2)	0.0490 (2)	0.0710 (10)
C(6)	0.0699 (2)	0.6023 (2)	0.0485 (2)	0.0700 (10)
C(7)	0.1106 (2)	0.5322 (2)	0.0998 (2)	0.0591 (8)
C(8)	0.1951 (1)	0.3757 (2)	0.1991 (1)	0.0479 (8)
C(9)	0.1698 (1)	0.2952 (2)	0.1424 (1)	0.0494 (8)
C(10)	0.1925 (2)	0.2891 (3)	0.0819 (2)	0.0658 (8)
C(11)	0.1657 (2)	0.2169 (3)	0.0272 (2)	0.0820 (10)
C(12)	0.1171 (2)	0.1499 (3)	0.0310 (2)	0.0810 (10)
C(13)	0.0927 (2)	0.1564 (2)	0.0887 (2)	0.0750 (10)
C(14)	0.1188 (2)	0.2288 (2)	0.1438 (2)	0.0601 (8)
C(15)	0.2750 (2)	0.4938 (3)	0.2816 (2)	0.0700 (10)
C(16)	0.2000 (2)	0.4430 (3)	0.4387 (2)	0.0930 (10)
C(17)	0.0781 (2)	0.2641 (3)	0.3665 (2)	0.0890 (10)
C(18)	0.2402 (2)	0.2442 (3)	0.3665 (2)	0.0960 (10)
C(19)	0.4280 (2)	0.3767 (3)	0.3462 (2)	0.1000 (10)
C(20)	0.3530 (2)	0.2191 (3)	0.2087 (2)	0.0900 (10)
C(21)	0.3701 (2)	0.4491 (3)	0.1618 (2)	0.0990 (10)

[a] $U_{eq} = {}^1/_3\sum_{i,j}U_{ij}a_i^*a_j^*\vec{a}_i\cdot\vec{a}_j$.

Table III. Bond Distances and Bond Angles for the Non-Hydrogen Atoms for [(AlMe$_3$)$_2${σ,σ-N,O-(MeN=C(Ph)C(Ph)=O)}] (1a)

(a) Bond Distances (Å)

Al(1)–N(1)	2.089 (2)	C(2)–C(3)	1.400 (3)
Al(1)–C(19)	1.966 (4)	C(2)–C(7)	1.393 (4)
Al(1)–C(20)	1.955 (4)	C(3)–C(4)	1.366 (5)
Al(1)–C(21)	1.955 (4)	C(4)–C(5)	1.373 (5)
Al(2)–O(1)	1.983 (2)	C(5)–C(6)	1.371 (6)
Al(2)–C(16)	1.944 (4)	C(6)–C(7)	1.367 (5)
Al(2)–C(17)	1.948 (4)	C(8)–C(9)	1.474 (3)
Al(2)–C(18)	1.955 (4)	C(9)–C(14)	1.385 (4)
O(1)–C(1)	1.238 (3)	C(9)–C(10)	1.398 (4)
N(1)–C(8)	1.276 (3)	C(10)–C(11)	1.369 (5)
N(1)–C(15)	1.471 (5)	C(11)–C(12)	1.370 (6)
C(1)–C(2)	1.445 (3)	C(12)–C(13)	1.371 (5)
C(1)–C(8)	1.520 (3)	C(13)–C(14)	1.374 (4)

(b) Bond Angles (deg)

N(1)–Al(1)–C(19)	101.7 (1)	Al(1)–N(1)–C(8)	133.1 (2)
N(1)–Al(1)–C(20)	110.4 (2)	Al(1)–N(1)–C(15)	109.3 (2)
N(1)–Al(1)–C(21)	98.7 (1)	C(8)–N(1)–C(15)	117.6 (3)
C(19)–Al(1)–C(20)	110.6 (2)	O(1)–C(1)–C(2)	122.2 (2)
C(19)–Al(1)–C(21)	115.2 (2)	O(1)–C(1)–C(8)	120.0 (2)
C(20)–Al(1)–C(21)	118.2 (2)	C(2)–C(1)–C(8)	117.7 (2)
O(1)–Al(2)–C(16)	98.2 (1)	C(1)–C(2)–C(3)	120.7 (2)
O(1)–Al(2)–C(17)	99.3 (1)	C(1)–C(2)–C(7)	120.9 (2)
O(1)–Al(2)–C(18)	107.1 (1)	N(1)–C(8)–C(9)	125.1 (2)
C(16)–Al(2)–C(17)	118.0 (2)	N(1)–C(8)–C(1)	121.9 (2)
C(16)–Al(2)–C(18)	116.4 (2)	C(1)–C(8)–C(9)	112.9 (2)
C(17)–Al(2)–C(18)	113.9 (2)	C(8)–C(9)–C(14)	121.1 (2)
Al(2)–O(1)–C(1)	142.0 (2)	C(8)–C(9)–C(10)	120.2 (3)

Compounds **2a–c**, which have been isolated as white crystalline solids, have according to elemental analyses[9] 2:1 Al/α-imino ketone stoichiometry. The ^1H and ^{13}C NMR spectra, which are discussed in ref 17b, are in agreement with structures consisting of a dimethylaluminum entity to which the (*E*)-imine–[R^{1}N=C(R^2)C(R^3,Me)O]$^-$ monoanion is bidentate bonded together with an oxygen-coordinated AlMe$_3$ monomer. Compounds **2** are soluble in the common aprotic solvents. Also these complexes are very air- and moisture-sensitive and decompose readily with moisture to give the new α-hydroxylimines.[17a] The reaction of the α-imino ketone *t*-BuN=CHC(Me)=O with Al$_2$Me$_6$, likewise in a 1:1 molar ratio, did not result in the formation of a stable analogue of the coordination complexes **1a** and **1b**. Instead methylation of the acetyl group, which is more reactive than the phenacyl group present in **1**, occurred (see eq 1) resulting in the formation of dialuminum complexes **2**.

Unambiguous proof for the molecular geometries of the novel compounds **1** and **2** in the solid came from X-ray structure determinations of **1a** and **2c**.

Molecular Geometry of [(AlMe$_3$)$_2${σ,σ-N,O-(MeN=(Ph)C(Ph)=O)}] (1a). Figure 2 gives an Ortep view of the molecule. Positional parameters and some bond lengths and angles with their esd's are listed in Tables II and III.[9]

The basic structural unit is the [(AlMe$_3$)$_2${σ,σ-N,O-(MeN=C(Ph)C(Ph)=O)}] molecule which consists of two AlMe$_3$ units linked together via a σ,σ-N,O-bridging α-imino ketone ligand. Each aluminum center is thus bonded covalently to the three methyl groups with aluminum–carbon bond lengths of 1.944–1.966 Å, which is in the range of such bonds in organoaluminum compounds,[18,20] and by one dative bond involving either one of the α-imino ketone heteroatoms (vide infra).

The Al(2)–O bond length (1.983 (2) Å) is likewise in the normal range (1.8–2.0 Å).[19] This distance is slightly shorter than the Al–O bonds observed in both Me$_3$Al·OEt$_2$ (2.014 (24) Å)[20] and (Me$_3$Al)$_2$·*p*-dioxane (2.02 (2) Å),[21] larger than that in *o*-tolyl$_3$Al·OEt$_2$ (1.928 (3) Å),[22] and equal to the value of the donor–acceptor bonds in [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$·2AlEt$_3$[23] (**3**). The C(1)–O–Al(2) bond is bent (142.0 (2)°) in a fashion similar to that found in **3** resulting in positions of the aluminum atom which are consistent with those expected on the basis of the disposition of the lone pairs at the oxygen atom. The Al(1)–N bond length (2.089 (2) Å) is among the longest reported organoaluminum–nitrogen bonds (normal range 1.90–2.02 Å)[24] and resembles the one (2.130 (5) Å) in [*i*-Bu$_2$AlOCH$_2$-2-C$_5$H$_4$N]$_2$, which contains two five-coordinate Al atoms.[25]

An interesting aspect of this novel type of α-imino ketone–metal complex is the observation that the α-imino ketone is bonded in the *Z* conformation at the C=N bond while the N=C(8)/C(1)=O torsion angle amounts to 85.9 (3)°. The imine bond length (N(1)=C(8) = 1.276 (3) Å) does not differ significantly from the corresponding distance in free PhH(Me)CN=C(Ph)C(Ph)=O (**4**) of 1.268 (2) Å,[26] but it is significantly smaller than this bond in *trans*-[PtCl$_2$(PEt$_3$){σ-N-(*t*-BuN=CHC(Me)=O)}] (**5**) (1.34 (4) Å).[6] The central C(1)–C(8) bond length of 1.520 (3) Å is comparable with that found in **4** (1.530 (2) Å and somewhat larger than the length of 1.44 (5) Å in **5**. The C(1)=O(1) bond length of 1.238 (3) Å is equal to that

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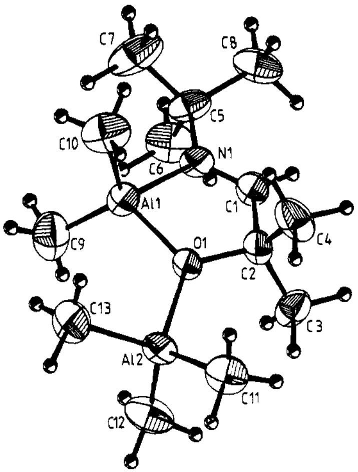

Figure 3. Ortep drawing of $Me_2Al(t\text{-}Bu)N{=}CHC(Me)_2OAlMe_3$(2c) (40% level). The adopted numbering scheme is indicated.

Table IV. Positional Parameters and U_{eq} Values for the Non-Hydrogen Atoms and Their Estimated Standard Deviations for [$Me_2Al(t\text{-}Bu)N{=}CHC(Me)_2OAlMe_3$] (2c)

atom	x/a	y/b	z/c	U_{eq},[a] Å^2
Al(1)	0.7659 (2)	0.2379 (2)	0.1526 (1)	0.0531 (8)
Al(2)	0.4236 (2)	0.2589 (2)	0.0545 (1)	0.0557 (8)
O(1)	0.5775 (5)	0.2953 (4)	0.1437 (2)	0.050 (2)
N(1)	0.7914 (6)	0.2795 (5)	0.2666 (3)	0.048 (1)
C(1)	0.6875 (8)	0.3382 (7)	0.2779 (4)	0.058 (2)
C(2)	0.5548 (8)	0.3652 (7)	0.2097 (4)	0.055 (2)
C(3)	0.4108 (8)	0.3342 (8)	0.2347 (4)	0.074 (2)
C(4)	0.563 (1)	0.4894 (7)	0.1884 (5)	0.084 (2)
C(5)	0.9198 (8)	0.2462 (8)	0.3336 (4)	0.063 (2)
C(6)	0.879 (1)	0.1352 (8)	0.3636 (5)	0.082 (2)
C(7)	1.0590 (9)	0.241 (1)	0.3001 (5)	0.108 (2)
C(8)	0.941 (1)	0.3358 (8)	0.3999 (5)	0.087 (2)
C(9)	0.767 (1)	0.0774 (9)	0.1410 (6)	0.095 (2)
C(10)	0.896 (1)	0.3339 (9)	0.1067 (5)	0.088 (2)
C(11)	0.2984 (9)	0.3925 (8)	0.0222 (4)	0.080 (2)
C(12)	0.317 (1)	0.1291 (9)	0.0855 (6)	0.091 (2)
C(13)	0.543 (1)	0.2219 (9)	−0.0265 (4)	0.087 (2)

[a] $U_{eq} = {}^1/_3\sum_{i,j}U_{ij}a_i{}^*a_j{}^*\vec{a}_i{\cdot}\vec{a}_j$.

found in 5 but somewhat longer than the corresponding distance in 4 of 1.209 (2) Å.

Molecular Geometry of $Me_2Al(t\text{-}Bu)N{=}CHC(Me)_2OAlMe_3$ (2c). Figure 3 gives an Ortep view of the molecule. Positional parameters and some bond lengths and angles with their esds are listed in Tables IV and V.[9]

The unit cell contains discrete molecules $Me_2Al(t\text{-}Bu)N{=}CHC(Me)_2OAlMe_3$ (2c). Its molecular geometry is very similar to those of $Me_2AlOC(Ph)N(Ph)CH(Me)OAlMe_3$[27] and $Me_2AlON(Me)NOAlMe_3$.[28] In all three compounds a dimethylaluminum unit is chelate bonded by a bidentate monoanionic ligand and a trimethylaluminum is coordinated to an oxygen atom of the ligand. The Al(1) center in 2c takes part in a five-membered AlNCCO ring of which the oxygen atom is covalently bonded to Al(1) and acts via the latter oxygen atom as a base toward Al(2). The values of the bond angles at N(1) and C(1) correspond to sp^2 hybridization which is reflected by the fact that the Al(1), N(1), C(5), C(1), and C(2) atoms are in one plane. However, the five-membered AlNCCO ring occurs in an envelope shape with O(1) as a flap (displacement from the least-squares plane amounts to −0.12 (2) Å).[29]

Table V. Bond Distances and Bond Angles for the Non-Hydrogen Atoms for [$Me_2Al(t\text{-}Bu)N{=}CHC(Me)_2OAlMe_3$] (2c)

(a) Bond Distances (Å)

Al(1)–N(1)	2.002 (6)	N(1)–C(1)	1.22 (1)
Al(1)–O(1)	1.825 (5)	N(1)–C(5)	1.521 (9)
Al(1)–C(9)	1.91 (1)	C(1)–C(2)	1.54 (1)
Al(1)–C(10)	1.93 (1)	C(2)–C(3)	1.51 (1)
Al(2)–O(1)	1.910 (5)	C(2)–C(4)	1.53 (1)
Al(2)–C(11)	1.97 (1)	C(5)–C(7)	1.50 (1)
Al(2)–C(12)	1.95 (1)	C(5)–C(6)	1.49 (1)
Al(2)–C(13)	1.995 (8)	C(5)–C(8)	1.55 (1)
O(1)–C(2)	1.460 (8)		

(b) Bond Angles (deg)

O(1)–Al(1)–N(1)	84.6 (2)	Al(1)–N(1)–C(5)	127.1 (5)
N(1)–Al(1)–C(9)	110.3 (4)	C(1)–N(1)–C(5)	121.6 (6)
N(1)–Al(1)–C(10)	107.7 (4)	N(1)–C(1)–C(2)	120.4 (7)
O(1)–Al(1)–C(9)	112.9 (4)	C(3)–C(2)–C(4)	113.3 (7)
O(1)–Al(1)–C(10)	113.2 (4)	O(1)–C(2)–C(4)	109.7 (6)
C(9)–Al(1)–C(10)	121.8 (5)	O(1)–C(2)–C(1)	105.5 (6)
O(1)–Al(2)–C(11)	109.5 (3)	O(1)–C(2)–C(3)	111.0 (6)
O(1)–Al(2)–C(12)	106.3 (3)	C(1)–C(2)–C(3)	108.7 (6)
O(1)–Al(2)–C(13)	101.7 (3)	C(1)–C(2)–C(4)	108.4 (7)
C(11)–Al(2)–C(12)	114.9 (4)	C(6)–C(5)–C(7)	112.7 (8)
C(11)–Al(2)–C(13)	110.3 (4)	N(1)–C(5)–C(7)	107.2 (6)
C(12)–Al(2)–C(13)	113.2 (4)	N(1)–C(5)–C(8)	110.3 (7)
Al(1)–O(1)–Al(2)	120.3 (3)	C(6)–C(5)–C(8)	110.5 (7)
Al(1)–O(1)–C(2)	115.4 (4)	C(7)–C(5)–C(8)	109.4 (7)
Al(2)–O(1)–C(2)	124.2 (4)	N(1)–C(5)–C(6)	106.7 (6)
Al(1)–N(1)–C(1)	111.3 (5)		

The Al(2) atom has a slightly distorted tetrahedral geometry. The average value of the O–Al(2)–C(methyl) angles of 105.8° is smaller than that of C(methyl)–Al(2)–C(methyl), 112.8°. These observations are similar to those in related complexes.[21] It has been found that large C–Al–D (D = donor group) angles are associated with the stronger donor–acceptor complexes Me_3Al–D.[30]

The Al(1) atom has a much more distorted tetrahedral geometry than Al(2). The maximum and minimum bond angles around the Al(1) atom are 121.8(5)° for C(9)–Al(1)–C(10) and 86.4 (2)° (bite angle) for N–Al(1)–O, respectively. The large difference arises from the constraints brought about by the specific bond angles in the chelating bidentate monoanionic ligand, which results in a specific value for the bite angle being invariably smaller than 90°. Both Al–O distances of 1.825 (5) and 1.910 (5) Å are comparable with the values observed in other terminal and μ-oxo bonds.[19b] The dative Al–N bond (2.002 (6) Å) is in accord with the value of 2.02 (1) Å found in (acetonitrile)trimethylaluminum[30] and with the value of 2.005 (3) Å found in $Al_2Me_5(NPh_2)$.[31] Recently, we found that a N–Al bond, in which the Al center is five-coordinate, e.g., in $[i\text{-}Bu_2AlOCH_2\text{-}2\text{-}C_5H_4N]_2$, is significantly longer (2.130 (5) Å).[25]

Comparison of Free and Coordinated α-Imino Ketone Ligands. It is interesting to compare the structure of the present compound 1a with the two other known, i.e., with that of PhH(Me)CN=C(Ph)C(Ph)=O (4) and of *trans*-$[PtCl_2(PEt_3)\{\sigma\text{-}N\text{-}(t\text{-}BuN{=}CHC(Me){=}O)\}]$ (5). The similarity in these structures is the near orthogonality of the N=C and the C=O groups (viz., the torsion angles in

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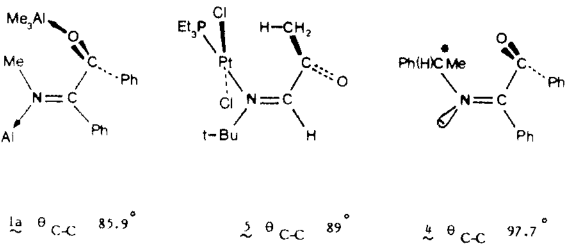

Figure 4. Structures of free and coordinated α-imino ketones: **1a**, 4e, σ-N, σ-O bridging, (*Z*)-imine, torsion angle = 85.9°; **5**, 2e, σ-N; (*E*)-imine, torsion angle = 89°; 4, free ligand; (*Z*)-imine, torsion angle = 97.7°.

1a, 85.9 (3)°, 4, 97.7 (2)°, and **5**, 85.9 (3)°) which seem to be independent of the nature of both the ligand substituents and whether or not the ligand is coordinated to a metal center. These observations suggest that the stable configurations of both free, σ-N monodentate and σ,σ-N,O bridging bonded α-imino ketones is the one with near orthogonality between the two chromofores. The conformational isomerism (*E* or *Z*) about the imine double bond then depends on the ligand substituents and on the coordinated metal (see Figure 4). Taking into account that the barrier to pyramidal inversion at the N center in the free ligand is only about 15 kcal/mol,[32-34] it is not necessary that the most favorable conformation found in metal complexes is the same as that in the corresponding free ligands.

Butadiene itself has been found to be planar trans.[35] The substituted butadienes have been found to be either planar trans or nonplanar gauche.[36] The molecules with nonplanar gauche conformations are those in which large steric interactions between atoms substituted at the 1- and 3- or 2- and 4-positions discourage the planar conformation. Electron diffraction studies for 2,3-dichloro-1,3-butadiene included identification of a higher energy nonplanar gauche conformation in the presence of a lower energy planar trans form.[37] The isoelectronic molecules 2,3-dimethylbutadiene and 2,3-butanedione (biacetyl) have similar bond configurations and are observed only in the planar trans form, in the case of 2,3-butanedione even at sample temperatures up to 520 °C.[38]

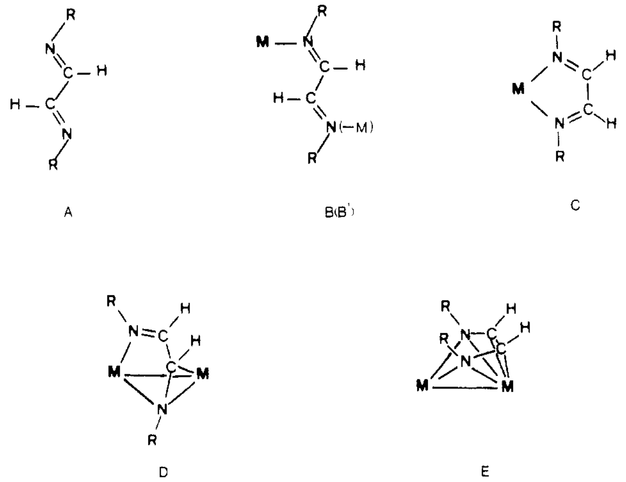

Figure 5. Structures of free and coordinated α-diimines: A, free ligand, *E-trans-E*, torsion angle (θ) = 0°;[40] B, 2e, σ-N, *E-trans-E*, θ = 0°;[40] B′, 4e, σ-N, σ-N′, bridging, θ = 0°;[39] C, 4e, σ-N, σ-N′, chelating, *E-cis-E*, θ = 5°;[41] D, 6e, σ-N, σ-N′, η^2-C=N′, (*E*)-imine, θ = 12.2°;[42] E, 8e, σ-N, σ-N′, η^2-C=N, η^2-C′=N′, θ = 0°.[43]

Recent studies[39] in our laboratory have shown that free 1,4-diaza-1,3-butadiene (R-DAB) molecules as well as coordinated R-DAB possess a nearly flat ligand skeleton with a (N=)CC(=N) torsion angle in the range of 0° (A) to 12° (D). This is shown in Figure 5 for various complexes in which the R-DAB ligand donates an increasing number of electron pairs going from compounds A to E.

The conformations of the free as well as of the coordinated α-imino ketones (see Figure 4) contrast with the conformations of the above discussed 1,4-dihetero-1,3-butadienes. The present information suggests that the nonplanarity of the 1-aza-4-oxo-1,3-butadiene ligand skeleton is the result of the search for a balance between the conformation with minimal steric interaction between the skeleton substituents (the nonplanar gauche conformation) and maximum resonance energy (the planar conformation). Our observations that the nonplanar gauche conformation of the α-imino ketones is the lower energy form are consistent with the absence of a good overlap in the bonding molecular orbitals ψ_1 and ψ_2 between the central carbon atoms because of the asymmetry of the molecule.

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Registry No. **1a**, 101859-60-3; **1b**, 101859-61-4; **2a**, 101859-62-5; **2b**, 101859-63-6; **2c**, 101859-64-7; Al_2Me_6, 15632-54-9; Me–C-(Ph)C(Ph)=O, 53601-37-9; *i*-PrN=C(Ph)C(Ph)=O, 75136-53-7; *t*-BuN=C(H)C(Me)=O, 67122-50-3.

Supplementary Material Available: Tables of positional and thermal parameters for all atoms, observed and calculated structure factors, and bond lengths and bond angles (Tables SI and SII) for $[(AlMe_3)_2\{\sigma,\sigma\text{-N,O-(MeN=C(Ph)C(Ph)=O)}\}]$ and $Me_2Al(t\text{-Bu})N{=}CHC(Me)_2OAlMe_3$ and a table of analytical data for **1a,b** and **2a–c** (Table SIII) (36 pages). Ordering information is given on any current masthead page.

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