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THE DOUBLE INSERTION OF *t*-BUTYL ISOCYANIDE BY TRIS(TETRAMETHYLCYCLOPENTADIENYL)ALUMINUM TO FORM $(\eta^1\text{-}C_5Me_4H)_2\overline{Al\{C(=NtBu)\text{—}C(=N}tBu)(C_5Me_4H)\}$*

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Abstract—Tris(tetramethylcyclopentadienyl)aluminum, Cp'_3Al ($Cp' = C_5Me_4H$), reacts with *t*-butyl isocyanide to form $(\eta^1\text{-}C_5Me_4H)_2\overline{Al\{C(=NtBu)\text{—}C(=N}tBu)(C_5Me_4H)\}$ which results from the double insertion of the isonitrile at a single Al-cyclopentadienyl ring position. Double isonitrile insertion occurs in preference to a single insertion such that only unreacted Cp'_3Al and the title compound are observed when fewer than two equivalents of the isonitrile are consumed. The molecular structure of $(\eta^1\text{-}C_5Me_4H)_2\overline{Al\{C(=NtBu)\text{—}C(=N}tBu)(C_5Me_4H)\}$ has been determined by single-crystal X-ray diffraction. The aluminum center is tetracoordinate with two η^1-cyclopentadienyl rings and the coupled isonitrile fragment bonding through a carbon of one iminoacyl group and a nitrogen of the other to form a four-membered azametallacycle.

Due to aluminum's strong Lewis acidity, the organometallic chemistry of aluminum exceeds the "Grignard-like" behavior of other main group metals and in many ways resembles the chemistry of the high valent, electrophilic, early transition metals.[1] The versatile manner in which aluminum activates unsaturated, carbon-containing substrates such as olefins, alkynes, carbonyl species and nitriles makes organoaluminum compounds especially useful in organic synthesis.[2] While the reaction chemistry of alkylaluminum compounds has been examined extensively toward this end, the chemistry of cyclopentadienylaluminum compounds has been virtually unexplored. We recently demonstrated a convenient synthesis of dicyclopentadienylaluminum alkyl and tricyclopentadienylaluminum compounds by reacting magnesocene with the appropriate aluminum chloride starting material.[3] We have now used this same chemistry to prepare tris(tetramethylcyclopentadienyl)aluminum, hereafter referred to as Cp'_3Al. This compound, upon treatment with *t*-butyl isocyanide, underwent an unexpected double insertion reaction to form $(C_5Me_4H)_2\overline{Al\{C(=NtBu)\text{—}C(=N}tBu)(C_5Me_4H)\}$, the molecular structure of which is presented herein.

RESULTS

Synthesis of Cp'_3Al

Unlike the parent compound Cp_3Al ($Cp = C_5H_5$), which is isolated as an oil from the reaction of magnesocene with $AlCl_3$,[3] Cp'_3Al may be isolated as a white, crystalline solid from an

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* Dedicated to Professor John E. Bercaw on the occasion of his 50th birthday.

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analogous reaction employing $(C_5Me_4H)_2Mg$ (eq. 1), albeit in more modest yields (see Experimental section).

$$3/2\,(C_5Me_4H)_2Mg + AlCl_3 \longrightarrow Cp'_3Al \quad (1)$$

The ^1H NMR spectrum of this compound is very simple with two singlets belonging to the two inequivalent pairs of methyl substituents on the cyclopentadienyl rings and a resonance corresponding to the allylic protons. The ^{13}C NMR pattern is consistent with the ^1H spectrum. Due to the high fluxionality of cyclopentadienylaluminum compounds in solution, their NMR spectra do not reflect the structures of these compounds in the solid state.[4] X-ray diffraction data were collected on a single crystal of Cp'_3Al. Unfortunately, the number of reflections were insufficient for a suitable refinement of the molecular structure. We will continue to pursue an X-ray data set on this compound suitable for a molecular structure determination.

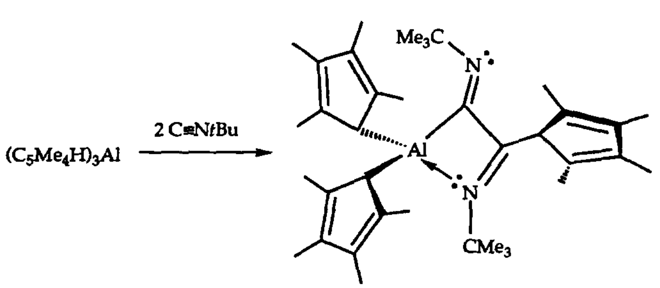
Cp'_3Al is the second reported example of a homoleptic cyclopentadienylaluminum compound. Cp_3Al was originally reported in the patent literature as a solid (m.p. 55–60°C) resulting from the reaction of bis(cyclopentadienyl)mercury with elemental aluminum.[5] We have also prepared Cp_3Al from magnesocene and $AlCl_3$; however, we consistently isolate this compound as an oil. It forms a solid upon complexation of a Lewis base such as *t*-butyl isocyanide, and we were able to determine the single-crystal X-ray structure of $(\eta^1\text{-}C_5H_5)_3Al(CNtBu)$.[3] With the molecular structure of $Cp_3Al(CNtBu)$ in hand, we decided to form the *t*-butyl isocyanide adduct of Cp'_3Al for comparison. In contrast to Cp_3Al, Cp'_3Al undergoes an insertion reaction with the isonitrile, the nature of which is described below.

Reaction of Cp'_3Al *with t-butyl isocyanide*

When a sample of Cp'_3Al in benzene-d_6 was treated with one equivalent of *t*-butyl isocyanide and examined by ^1H NMR, the two peaks belonging to the methyl substituents on the cyclopentadienyl rings became significantly broadened although the chemical shift of neither peak changed perceptibly. This behavior can perhaps be attributed to the reversible binding of the isonitrile by the aluminum complex. Over time the solution became pink as a new species began to appear in the ^1H NMR spectrum. After 2 h the solution was a deep burgundy color, the original ^1H resonance from the *t*-butyl isocyanide had disappeared and two new peaks of equal instensity were present in that region of the spectrum. New peaks for the methyl substituents on the cyclopentadienyl rings and two new allylic hydrogen peaks with a 2 : 1 ratio of intensities also appeared. Interestingly, half of the Cp'_3Al starting material was still present; thus, two equivalents of the isonitrile per aluminum had been consumed. The ^{27}Al NMR of the product revealed that it corresponded to a single new aluminum species. This new compound can be isolated as a pale orange solid from the reaction of two equivalents of *t*-butyl isocyanide with Cp'_3Al. The infrared spectrum of this new compound displayed no bands in the isonitrile $\nu(C{\equiv}N)$ region but did reveal a band at 1535 cm^{-1}, which is within the range of $\nu(C{=}N)$ stretching frequencies for an iminoacyl group.[6] Based on this information, it was clear that both isonitriles had been inserted by Cp'_3Al. A single crystal X-ray structure determination of the compound revealed that, in fact, both isonitriles had been inserted at a single Al-cyclopentadienyl position to form $(C_5Me_4H)_2Al\{C({=}NtBu){-}C({=}NtBu)(C_5Me_4H)\}$ (eq. 2).

Molecular structure of $(\eta^1\text{-}C_5Me_4H)_2Al\{C({=}NtBu){-}C({=}NtBu)(C_5Me_4H)\}$

An ORTEP drawing of the molecule is shown in Fig. 1. Selected bond lengths and angles are pre-



(2)

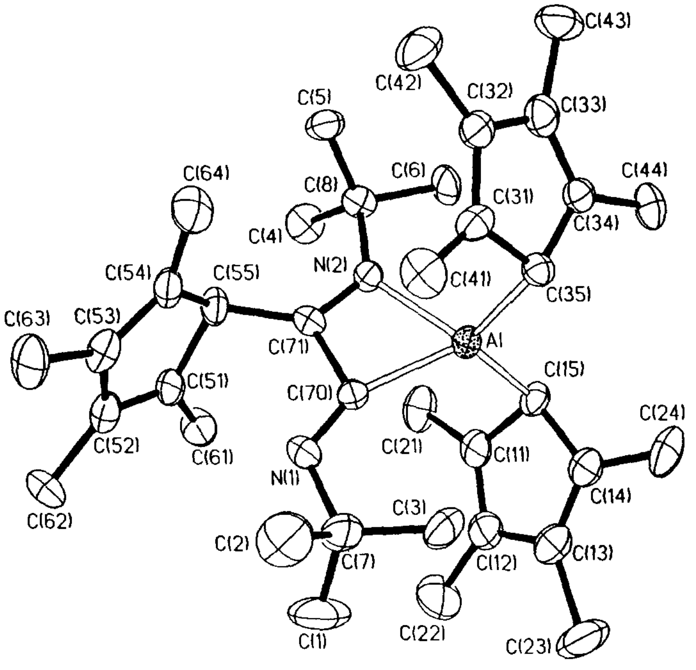


Fig. 1. ORTEP drawing of the molecular structure of $(\eta^1\text{-C}_5\text{Me}_4\text{H})_2\text{Al}\{\text{C}(=\text{N}t\text{Bu})\text{—C}(=\text{N}t\text{Bu})(\text{C}_5\text{Me}_4\text{H})\}$. Thermal ellipsoids are shown at the 30% probability level.

sented in Table 1. Inspection of the bond lengths and bond angles reveal that the diimine fragment from the coupled isonitriles coordinate the aluminum through C(70) and the lone pair of N(2) rather than coordinating C(70), C(71) and N(2) in an η^3 π-allyl fashion. This latter bonding arrangement is ruled out by the Al—C(71) interatomic separation of 2.509(12) Å, which is substantially longer than the corresponding Al—C(70) and Al—N(2) bond distances of 2.023(12) and 2.016(10) Å, respectively. The resultant four-membered ring is further characterized by a normal C(70)—C(71) bond of 1.526(17) Å with the imine N—C bonds [N(1)—C(70), 1.275(16) Å and N(2)—C(71), 1.291(15) Å] being consistent with double bonds.[6] The aluminum is therefore four-coordinate with a highly distorted tetrahedral geometry, the distortion due mainly to the geometric constraints of the diimine ligand. The C—C bond lengths in the cylopentadienyl rings directly coordinated to the aluminum reflect localized π-bonds, with the aluminum attached to the allylic carbon of each ring. Likewise, the inserted cyclopentadienyl ligand is connected to the diimine backbone through the allylic carbon.

In order to determine the strength of the bonding interaction between Al and N(2) and to determine if N(1) and N(2) could exchange positions, a sample of the compound in d_8-toluene was heated in the NMR probe. There was no apparent change in either the line widths or the chemical shifts of the N-*t*-butyl resonances in the ^{1}H NMR spectrum up to 65°C at which temperature the sample began to decompose. After 2 h at 70°C the ^{1}H NMR spectrum of the sample exhibited an ill-defined forest of peaks.

DISCUSSION

Surprisingly few reactions of aluminum compounds with isonitriles have been reported. While isonitrile insertion into an Al—H[7] and an Al—Cl[8] bond have been observed, no example of the insertion of an isonitrile into an Al—C bond has been reported let alone a double isonitrile insertion. The methylisonitrile adduct of trimethylaluminum has been prepared and the adduct remains intact even upon sublimation of the complex at 40°C.[8] Cp_3Al also forms simply an adduct with *t*-butyl isonitrile. The only other example of a multiple insertion by aluminum involves the double insertion of acetonitrile into aluminum amide bonds.[9]

This isonitrile insertion chemistry is better established among the transition metals.[10] A few examples of isonitrile insertion by lanthanide and actinide metal alkyl complexes have also been reported.[10a] Low valent nickel and palladium complexes offered the earliest examples of multiple isonitrile insertion into a metal–carbon bond.[11] The nickel systems are remarkable for their ability to

Table 1. Selected bond lengths (Å) and bond angles (°) for $(\eta^1\text{-}C_5Me_4H)_2\overline{Al\{C(=NtBu)-C}(=NtBu)(C_5Me_4H)\}$

Al—N(2)	2.016(10)	C(12)—C(13)	1.473(23)
Al—C(70)	2.023(12)	C(13)—C(14)	1.373(22)
Al—C(71)	2.509(12)	C(14)—C(15)	1.511(20)
Al—C(15)	2.038(12)	C(31)—C(32)	1.381(18)
Al—C(35)	2.046(11)	C(31)—C(35)	1.496(16)
N(1)—C(7)	1.479(19)	C(32)—C(33)	1.456(19)
N(1)—C(70)	1.275(16)	C(33)—C(34)	1.363(19)
N(2)—C(8)	1.511(16)	C(34)—C(35)	1.490(17)
N(2)—C(71)	1.291(15)	C(51)—C(52)	1.358(19)
C(70)—C(71)	1.526(17)	C(51)—C(55)	1.546(17)
C(55)—C(71)	1.517(16)	C(52)—C(53)	1.500(19)
C(11)—C(12)	1.354(22)	C(53)—C(54)	1.353(20)
C(11)—C(15)	1.530(18)	C(54)—C(55)	1.539(18)
N(2)—Al—C(15)	113.7(5)	Al—C(35)—C(34)	109.0(8)
N(2)—Al—C(70)	68.2(4)	C(7)—N(1)—C(70)	121.7(11)
N(2)—Al—C(35)	112.4(4)	C(8)—N(2)—C(71)	128.1(10)
N(2)—C(71)—C(55)	128.5(11)	C(11)—C(15)—C(14)	102.8(11)
N(2)—C(71)—C(70)	106.7(9)	C(15)—Al—C(35)	115.1(5)
Al—N(2)—C(71)	96.2(7)	C(15)—Al—C(71)	124.0(4)
Al—N(2)—C(8)	135.6(7)	C(15)—Al—C(70)	120.9(5)
Al—C(70)—C(71)	88.8(7)	C(31)—C(35)—C(34)	104.1(10)
Al—C(70)—N(1)	153.4(10)	C(35)—Al—C(70)	117.1(5)
Al—C(15)—C(11)	107.3(8)	C(35)—Al—C(71)	119.2(4)
Al—C(15)—C(14)	104.8(9)	C(55)—C(71)—C(70)	124.7(10)
Al—C(35)—C(31)	108.9(8)		

polymerize isonitriles. Examples of multiple isonitrile insertion by electrophilic, high valent, early transition metals probably offer a better comparison with aluminum, however. Teuben and coworkers found that the η^1-iminoacyl complexes resulting from the insertion of xylyl isocyanide into the M—CH_2 bonds of $(\eta^5\text{-}C_5Me_5)(\eta^5,\eta^1\text{-}C_5Me_4CH_2)MCl$ complexes [M = Ti, Zr] insert a second isocyanide molecule, coupling the isocyanide fragments in the same manner as described here for aluminum.[12] In fact, the mono-iminoacyl complexes decompose over time to form the double insertion product and the starting fulvene complexes via the deinsertion of the isocyanide, indicating that the coupled isocyanide product is more stable. Erker has demonstrated the insertion of alkyl isocyanides into the metal–carbon bond of (η^2-formaldehyde)zirconocene to form four-membered heterometallacycles similar to the aluminum azametallacycle except for the presence of oxygen in the four-membered ring which serves to couple two zirconium centers into a dimer.[13] Double isonitrile insertion to form a four-membered azametallacycle is observed upon treatment of $[(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2]^-$ with methyl iodide.[14] Although additional methylation of the exocyclic nitrogen produces an iminodimethylaminocarbene complex, the molybdenum complex still serves as a useful comparison with the aluminum metallacycle. In this case, a clear distinction between the aluminum and the transition metal can be drawn. Unlike the molybdenum, which coordinates both the carbon and nitrogen of the imine in a π-type interaction presumably through the involvement of a *d* orbital, the aluminum can coordinate only the nitrogen lone pair of the internal imine through the use of its formally vacant *p* orbital. A four-membered metallacyclic structure analogous to that of the aluminum compound has been proposed for the iron double isonitrile insertion product formed in the reaction of $Fe(tBuNC)_5$ with MeI.[15] This structural assignment was based solely on spectroscopic data, however. As with the iron system, a single-insertion iminoacyl intermediate is not detected in the formation of the title aluminum compound. Rather, the second isonitrile insertion is so much faster than the first that only the double insertion product and Cp'_3Al are present in the reaction mixture when fewer than two equivalents of isonitrile are consumed. Rothwell and coworkers reported the formation of a titanium "tris-insertion" compound from the reaction of a Ti^{IV} mono-iminoacyl species with isonitrile.[16] This "tris-insertion" product presumably arises from the intramolecular coupling reaction of an intermediate possessing both a diimine group from a double-isonitrile insertion and an iminoacyl group from a single insertion. In this case, the single-insertion and tris-insertion compounds are isolable, but the double-insertion intermediate is not detected.

The greater reactivity of Cp'_3Al relative to the parent Cp_3Al can probably be attributed to steric labilization of the aluminum–carbon bonds in the former complex. This effect of sterics on isonitrile insertion activity has been illustrated by Lappert with the zirconocene mixed alkyl complex $(\eta^5\text{-}C_5H_5)_2Zr(Me)\{CH(SiMe_3)_2\}$, which inserts the isocyanide selectively at the more hindered alkyl position.[17]

There was no apparent reaction between Cp'_3Al and carbon monoxide upon exposing a C_6D_6 solution of the aluminum compound to an atmosphere of CO in a sealed NMR tube and examining the sample by ^1H NMR. We plan to examine the reactivity of Cp'_3Al toward other unsaturated, small molecules such as nitriles, isocyanates, carbonyl compounds, CO_2, CS_2 and SO_2. In addition, we are presently trying to prepare the bulkier, permethylated complex, $(C_5Me_5)_3Al$, in order to investigate further the effect of sterics on the reactivity of tricyclopentadienylaluminum compounds.

EXPERIMENTAL

General considerations

All manipulations were performed using a combination of glovebox, high-vacuum or Schlenk techniques. All solvents were distilled under nitrogen over sodium benzophenone ketyl (toluene, methylcyclohexane, petroleum ether). The dried solvents were stored in line-pots from which they were either vacuum transferred from sodium benzophenone ketyl or cannulated directly. NMR solvents: benzene-d_6 and chloroform-d were dried over activated 4 Å molecular sieves. Argon was purified by passage over oxy tower BASF catalyst (Aldrich) and 4 Å molecular sieves. Aluminum trichloride (Aldrich) was sublimed prior to use. *t*-Butyl isocyanide was used as received from Aldrich. 2,3,4,5-Tetramethyl-1,2-cylopentenone was prepared as described in the literature[18] or was purchased from Aldrich. The ketone was converted to tetramethylcyclopentadiene by reduction with $LiAlH_4$, followed by acid-catalyzed dehydration as described by Marks and coworkers.[12]

NMR spectra were recorded on an IBM NR-300 (300.13 MHz ^1H, 74.43 MHz ^{13}C, 78.206 MHz ^{27}Al) and an IBM NR-200 (200.13 MHz ^1H, 50.327 MHz ^{13}C, 52.148 MHz ^{27}Al). All chemical shifts are reported in ppm and referenced to solvent (^{13}C, ^1H) or $Al(OH)_3$ (^{27}Al, external reference, δ 0 ppm). Elemental analyses were determined by Desert Analytics (Tucson, Arisona, U.S.A.) and the University of Idaho analytical facilities.

Preparation of $(C_5Me_4H)_2Mg$

The preparation of $(C_5Me_4H)_2Mg$ is analogous to the original preparation described for magnesocene.[19] Tetramethylcyclopentadiene (20 g, 0.16 mol) was added dropwise by syringe to 82 cm^3 of a 1 M solution of dibutylmagnesium in hexane cooled by an ice/water bath. The reaction was stirred at room temperature for 12 h and then cooled to −78°C to afford a white microcrystalline solid which was filtered cold (yield: 11 g, 49%). The yellow oil left behind after the removal of solvent from the filtrate was found by ^1H NMR to contain product contaminated with excess dibutylmagnesium. Redissolution of the oil in petroleum ether and cooling to −78°C did not afford a second crop of product. ^1H NMR (C_6D_6): δ 5.48 (s, 1, $\{C_5(CH_3)_4\mathit{H}\}$), 2.00, 1.91 (2s, 12, $\{C_5(C\mathit{H}_3)_4H\}$). Calc. for $C_{18}H_{26}Mg$: C, 81.06; H, 9.83. Found: C, 80.83; H, 9.65%.

Preparation of $(C_5Me_4H)_3Al$

Toluene (25 cm^3) was added to a mixture of $AlCl_3$ (0.895 mg, 6.71 mmol) and $(C_5Me_4H)_2Mg$ (2.87 g, 10.8 mmol) and the reaction mixture was heated to *ca* 50°C for 1 h with stirring and then stirred for another 2 h at room temperature. The resulting $MgCl_2$ precipitate was removed by filtration. The toluene was removed from the filtrate, and the residue was dissolved in 20 cm^3 petroleum ether and cooled to −78°C to afford a white, crystalline solid (yield after 2 crops: 0.95 g, 36%). The residue obtained after stripping the solvent from the mother liquor was found by ^1H NMR to contain some of the product along with ill-defined decomposition products. ^1H NMR (C_6D_6): δ 3.37 (s, 1, $C_5(CH_3)_4\mathit{H}$), 2.01, 1.95 (2s, 12, $C_5(C\mathit{H}_3)_4H$). ^{13}C NMR (C_6D_6): δ 132.4, 122.9 ($\mathit{C}_4(CH_3)_4CH$), 70.61 ($C_4(CH_3)_4\mathit{C}H$), 13.36, 11.55 ($C_4(\mathit{C}H_3)_4CH$). ^{27}Al NMR (C_6D_6): δ 65. Calc. for $C_{27}H_{39}Al$: C, 83.0; H, 10.1. Found: C, 83.4; H, 10.8%.

Preparation of $(\eta^1\text{-}C_5Me_4H)_2\overline{Al\{C({=}N\mathit{t}Bu){-}C({=}N}\,\mathit{t}Bu)(C_5Me_4H)\}$

t-Butyl isocyanide (0.33 cm^3, 2.9 mmol) was condensed into a solution of $(C_5Me_4H)_3Al$ (570 mg, 1.46 mmol) in 30 cm^3 toluene cooled at -78°C. The reaction was warmed to room temperature and stirred for 5 h. The reaction solution turned from colorless to pink over time and finally became a dark burgundy color. The toluene was removed under vacuum, and the residue was was taken up in *ca* 10 cm^3 heptane and cooled at -78°C to precipitate a light orange powder which was collected by cold filtration (yield: 452 mg, 56%). ^{1}H NMR (CDCl$_3$): δ 4.08 (s, 1, $C_5(CH_3)_4\mathit{H})C$, 3.56 (s, 1, $C_5(CH_3)_4\mathit{H})_2Al$), 2.13, 1.97, 1.81, 1.79, 1.69, 1.66 (4s, 36, $C_5(C\mathit{H}_3)_4H$), 1.40, 0.75 (2s, 18, $NC(C\mathit{H}_3)_3$). ^{13}C NMR (CDCl$_3$): δ 194 ($\mathit{C}NC(CH_3)_3$), δ 138.6, 132.5, 132.2, 131.8, 131.5 ($\mathit{C}_4(CH_3)_4CH$), 60.5, 59.5, 58.5, 56.7 ($C_4(CH_3)_4\mathit{C}H$ and $CN\mathit{C}(C\mathit{H}_3)_3$), δ 29.9, 28.0 ($NC(C\mathit{H}_3)_3$), δ 15.84, 15.80, 12.9, 11.9, 11.77, 11.2 ($C_4(\mathit{C}H_3)_4CH$). ^{27}Al NMR (C$_6$D$_6$): δ 60. An analytical sample was recrystallized from toluene. Calc. for $C_{37}H_{54}N_2Al$: C, 80.24; H, 9.83; N, 5.06. Found: C, 80.08; H, 10.15; N, 4.95%. IR data (Nujol mull, KBr plates, cm^{-1}): 1535(νC=N).

Crystal data

$C_{37}H_{57}AlN_2$, $M = 499.4$, monoclinic, space group P2$_1$/c, $a = 10.537(2)$, $b = 16.745(3)$, $c = 20.767(4)$ Å, $\beta = 96.52(3)$°, $V = 3640(2)$ Å^3, $Z = 4$, $D_c = 1.015$ Mg m^{-3}, $F(000) = 996$.

Data collection, structure solution and refinement

Dark red crystals of the compound were obtained from a toluene solution cooled at -60°C. A single crystal with dimensions $0.7 \times 0.2 \times 0.25$ mm was mounted in a glass capillary. The X-ray diffraction data were collected on a Syntex P2$_1$ diffractometer upgraded to Siemens P4 specifications using monochromatized Mo-K_α ($\lambda = 0.71073$ Å) radiation. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 50 reflections 41 of which were measured with a thin shell search ($27 < 2\theta < 30$°); 4753 independent reflections in the range $3.5 < 2\theta < 45$° were observed and of these 2235 with $F > 4.0\sigma(F)$ were used for the structure solution.

The structure was solved using a sharpened Patterson map, completed by subsequent difference Fourier syntheses and full-matrix least-squares refinement on F to minimize $\Sigma w(F_o - F_c)^2$ using the weighting scheme $w^{-1} = \sigma^2(F) + 0.001F^2$. All atoms were refined with anisotropic displacement coefficients. No hydrogens were introduced in order to conserve the data. In the final refinement cycle of 361 parameters the largest and mean Δ/σ values were 0.004 and 0.000 respectively. The refinement converged to $R = 0.1060$ and $wR = 0.1180$ for $|F| \geqslant 4\sigma$ with a goodness of fit of 3.79. The largest difference peak and difference hole were 0.42 and -0.030 e Å^{-3} in the final difference map.

All software and sources of the scattering factors are contained in either the SHELXTL (5.1) or the SHELXTL PLUS (4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

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