

Synthesis of a Bis(cyclopentadienyl)lanthanum Aryl Complex with a Pseudofacially Bound Bis(*ortho*)-Chelating Aryldiamine Ligand. X-ray Structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{La}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})$

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Summary: Reaction of $\text{Cp}_3\text{La}\cdot\text{THF}$ with $\text{Li}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})$ in benzene gave the first crystallographically characterized lanthanum aryl complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{La}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})$, in which the bis(*ortho*)-chelating aryldiamine ligand is bound in a pseudofacial "Cp-like" fashion.

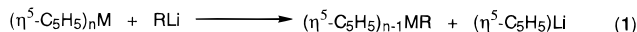
Introduction

With the rapid development of organolanthanide chemistry¹ over the past few decades, several complexes containing one or more aryl groups directly σ -bonded to middle and late lanthanide elements (Sm, Gd, Yb, Lu) have been isolated and their structure determined by X-ray crystallography.² In contrast, attempts to synthesize such complexes of early lanthanides like lanthanum itself generally have failed and only the "ate" complexes LiLaPh_4 and LiPrPh_4 have been reported.³ Recently, we have shown that the potentially terdentate, monoanionic aryldiamine ligand 2,6-bis[(dimethylamino)methyl]phenyl ($=\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6} = \text{NCN}$) and its derivatives of general formula $\text{C}_6\text{H}_3\{\text{CH}_2\text{NRR}'\}_2\text{-2,6}$ provide new leads in metal-mediated catalysis by controlling the reactivity of both early⁴ and late⁵ transition metal centers. This aryldiamine ligand can occupy a similar number of coordination sites and donate an

equivalent number of bonding electrons as the cyclopentadienyl ligand.⁶ We report here the synthesis and X-ray characterization of the first bis(cyclopentadienyl)lanthanum aryl complex, using this NCN ligand.

Results and Discussion

We have recently shown that NCN complexes of lanthanum could not be prepared from the reaction of LaCl_3 with $\text{Li}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})$, while for the smaller group 3 and lanthanide metals yttrium and lutetium the ate complexes $\text{MCl}_3(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})\text{-Li}(\text{THF})_2$ ($\text{M} = \text{Y, Lu}$) were obtained easily.⁷ However, the direct exchange of Cp groups for aryl (or alkyl) groups, as introduced by Lehmkuhl,⁸ appears to be an excellent procedure to mixed lanthanum cyclopentadienyl/aryl species. (see eq 1).



R = alkyl, aryl

By reaction of $\text{Cp}_3\text{La}\cdot\text{THF}$ ⁹ with 1 molar equiv of $\text{Li}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})$ in benzene at reflux temperature, $\text{La}(\text{C}_5\text{H}_5)_2(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})$ (**1**) is obtained as a white, air- and moisture-sensitive powder. Complex **1** is very soluble in aromatic and ethereal solvents, but insoluble in aliphatic solvents, and upon hydrolysis gives the parent diamine $\text{C}_6\text{H}_4\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6}$ and cyclopentadiene. When 2 equiv of $\text{Li}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})$ was reacted with $\text{Cp}_3\text{La}\cdot\text{THF}$ in an attempt to replace two cyclopentadienyl ligands, a 1:1 mixture of **1** and unreacted $\text{Li}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})$ was isolated after heating at reflux in benzene for 18 h.

Crystals for an X-ray analysis of **1** were grown by cooling a toluene solution to -30°C . The structure determination shows **1** to consist of a lanthanum ion, surrounded by two η^5 -coordinated cyclopentadienyl

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(1) The term lanthanides is used as including the Group 3 metals yttrium and lanthanum.

(2) *Sm*: Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112. *Gd*: (a) Lin, G.-Y.; Jin, Z.-S.; Zhang, Y.-M.; Chen, W.-Q. *J. Organomet. Chem.* **1990**, *396*, 307. (b) Lin, G.-Y.; Jin, Z.-S.; Zhang, Y.-M.; Chen, W.-Q. *Jiegou Huaxue (J. Struct. Chem.)* **1991**, *10*, 192. *Yb*: (a) Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Yu. F.; Zakharov, L. N.; Struchkov, Yu. T. *J. Organomet. Chem.* **1991**, *421*, 29. (b) Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Yu. F.; Zakharov, L. N.; Struchkov, Yu. T. *J. Organomet. Chem.* **1992**, *429*, 27. *Lu*: (a) Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194. (b) Wayda, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1984**, *3*, 939. (c) Wayda, A. L.; Rogers, R. D. *Organometallics* **1985**, *4*, 1440. (d) Cotton, S. A.; Hart, F. A.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1225.

(3) Hart, F. A.; Massey, A. G.; Saran, M. S. *J. Organomet. Chem.* **1970**, *21*, 147.

(4) Abbenhuis, H. C. L.; Feiken, N.; Haarman, H. F.; Grove, D. M.; Horn, E.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 2227.

(5) (a) Grove, D. M.; van Koten, G.; Verschuuren, A. H. M. *J. Mol. Catal.* **1988**, *45*, 169. (b) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659.

(6) (a) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681. (b) Abbenhuis, H. C. L.; Feiken, N.; Grove, D. M.; Jastrzebski, J. T. B. H.; Kooijman, H.; van der Sluis, P.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9773.

(7) Hogerheide, M. P.; Grove, D. M.; Boersma, J.; Jastrzebski, J. T. B. H.; Kooijman, H.; Spek, A. L.; van Koten, G. *Chem. Eur. J.* **1995**, *1*, 343.

(8) Lehmkuhl, H.; Danowski, F.; Benn, R.; Mynott, R.; Schroth, G. *Chem. Ber.* **1986**, *119*, 2542.

(9) $(\text{C}_5\text{H}_5)_3\text{La}\cdot\text{THF}$ was synthesized using a simplified procedure, omitting the use of excess NaC_5H_5 and sublimation (Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383) or Soxhlet extraction with toluene (Jacob, K.; Glanz, M.; Tittes, K.; Thiele, K.-H.; Pavlik, I.; Lyczak, A. *Z. Anorg. Allg. Chem.* **1989**, *577*, 145); see Experimental Section.

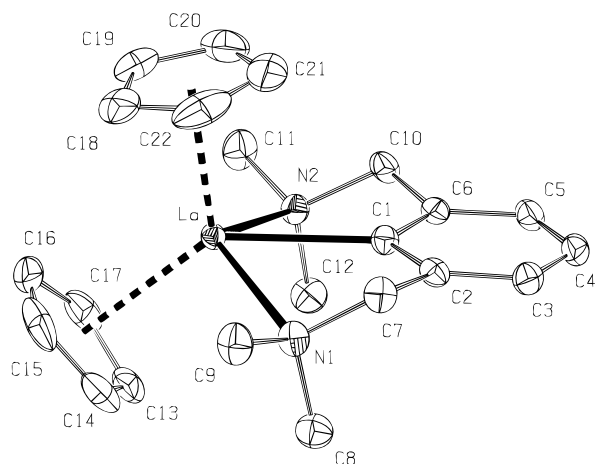


Figure 1. ORTEP representation (50% probability) of La-(C₅H₅)₂(C₆H₃{CH₂NMe₂}₂-2,6) (**1**) with the adopted numbering scheme. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for La(C₅H₅)₂(C₆H₃{CH₂NMe₂}₂-2,6) (1**)^a**

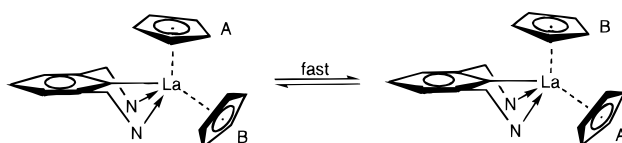
Distances			
La-C(1)	2.548(3)	La-C(16)	2.926(5)
La-N(1)	2.788(3)	La-C(17)	2.868(4)
La-N(2)	2.755(3)	La-C(18)	2.785(4)
La-cent(1)	2.632(2)	La-C(19)	2.805(4)
La-cent(2)	2.572(2)	La-C(20)	2.844(5)
La-C(13)	2.849(5)	La-C(21)	2.871(6)
La-C(14)	2.868(5)	La-C(22)	2.835(4)
La-C(15)	2.921(5)		
Angles			
N(1)-La-N(2)	121.98(9)	C(1)-La-cent(2)	98.74(9)
C(1)-La-cent(1)	139.87(9)	cent(1)-La-cent(2)	121.38(7)

^a Cent(1): C(13)-C(17). Cent(2): C(18)-C(22).

ligands and a pseudofacial, *N,C,N*-coordinated aryl-diamine ligand (see Figure 1 and Table 1). The geometry of the anionic binding sites of the ligands [cent(1) and cent(2)] of the cyclopentadienyl rings and C_{ipso} of NCN] around the lanthanum ion is distorted trigonal planar [the sum of the angles in the trigonal plane = 359.99(9)° with La 0.003(1) Å out of this plane]. This planar arrangement of negative charges around the La³⁺ cation is in agreement with the ionic nature of the metal-ligand bonds in organolanthanide complexes. The anionic binding sites are not regularly distributed around La³⁺, as the angles in the trigonal plane vary from 98.74(9)° (C(1)-La-cent(1)) to 139.87(9)° (C(1)-La-cent(2)) and 121.38(7)° (cent(1)-La-cent(2)). Whereas the latter angle has a value close to that expected for a regular trigonal arrangement, the larger C(1)-La-cent(2) angle is caused by the pseudofacial coordination of the nitrogen atoms of the NCN ligand to lanthanum. This causes an unequivalence between the two cyclopentadienyl ligands in the solid state that is reflected in their distances to lanthanum [La-cent(1) = 2.572(2) Å; La-cent(2) = 2.632(2) Å].

The La-N bond lengths of 2.788(3) and 2.755(3) Å in **1** are considerably shorter than the La-N bond length in (Me₂NCH₂CH₂C₅H₄)₃La¹⁰ (2.898(6) Å) and that in the mixed-metal complex LaCu₂(bdmap)₃(O₂CCF₃)₄¹¹ (2.85-

Scheme 1. Interconversion between the Two Stereoisomers of **1 in Solution**



(2) Å; Hbdmap = 1,3-bis(dimethylamino)propan-2-ol). The rather acute N-La-N angle of 121.98(9)° is due to the interconnectedness of the binding sites in NCN. This N-La-N angle is smaller than the N-Lu-N angle of 123.1(6)° in [Lu(*μ*-Cl)(C₆H₃{CH₂NMe₂}₂-2,6)(CH₂-SiMe₃)₂]₂,⁷ which also contains NCN in a pseudofacial coordination mode. The La-C(1) bond length in **1** is much longer at 2.548(3) Å than the Lu-C bond of 2.32(3) Å in the lutetium complex, reflecting the larger size of the lanthanum ion as compared to the lutetium ion (1.032 Å vs 0.861 Å).

Complex **1** shows simple ¹H NMR spectra with singlets for the NMe₂, CH₂N, and C₅H₅ resonances over the temperature range 175–380 K. At room temperature, ¹³C NMR spectra also show all expected resonances as singlets, except that of the *ipso*-carbon, which is too broad to be observed. Because the signal for the benzylic protons appears as a singlet, it must be concluded that **1** is highly fluxional in solution and has one apparent molecular plane of symmetry running through C(4), C(1), La, and both centroids of the cyclopentadienyl rings, as well as a second one containing the two benzylic carbon atoms (see Scheme 1). In addition, a fast dissociation/association process (arm off/on) of the N-La donative bonds, in combination with pyramidal inversion at nitrogen and rotation about the CH₂-N bond, would render the methyl groups on nitrogen homotopic as observed.

The apparently symmetric solution structure of the cyclopentadienyl rings, which are asymmetrically bound in the solid state, also indicates that low-energy fluxional processes are operative in solution that make all prochiral groups of **1** homotopic on the NMR time scale. A likely process involves a flip in the C(1),cent(1),cent(2) trigonal plane which would render the diastereotopic atoms enantiotopic and is likely to be of low energy (see Scheme 1). Another explanation, i.e. a fast dissociation/association process (arm off/on) of the La-N coordinate bonds, seems to be less probable in view of the high Lewis acidity of the La³⁺ center.

Experimental Section

General Methods. The reactions were performed using standard Schlenk techniques in an atmosphere of dry, oxygen-free dinitrogen. All solvents were carefully dried and distilled prior to use. Anhydrous LaCl₃ was purchased from Strem Chemicals, Inc. Salt- and solvent-free 2,6-bis[(dimethylamino)methyl]phenyl]lithium was synthesized according to a literature procedure.¹² NaCp was synthesized from sodium sand and cyclopentadiene in THF at room temperature, followed by careful removal of all solvent at 80 °C under vacuum. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim, Germany (C, H, N), or at Delft University of Technology, Laboratory of Materials Science (Na). ¹H and ¹³C NMR data were collected on a

(10) Anwander, R.; Herrmann, W. A.; Scherer, W.; Munck, F. C. *J. Organomet. Chem.* **1993**, *462*, 163.

(11) Wang, P.; Pang, Z.; Smith, K. D. L.; Wagner, M. J. *J. Chem. Soc., Dalton Trans.* **1994**, 955.

(12) van Koten, G.; Leusink, A.; Noltes, J. G. *J. Chem. Soc., Chem. Commun.* **1970**, 1107.

Table 2. Crystallographic Data for 1

formula	C ₂₂ H ₂₉ N ₂ La	Z	4
fw	460.39	μ , cm ⁻¹	21.3
space group	P2 ₁ 2 ₁ 2 ₁ (No. 19)	T, K	150
cryst system	orthorhombic	radiation;	Mo K α ; 0.710 73
a, Å	8.8503(6)	λ , Å	(graphite monochromator)
b, Å	14.8004(17)	final R ^a	0.023 [6137,
c, Å	15.3835(11)		I ₀ > 2.5 σ (I ₀)
V, Å ³	2015.1(3)	final R _w ^b	0.025
D _{calc} , g cm ⁻³	1.517	S	1.45

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum [w(|F_o| - |F_c|)^2 / \sum [w(F_o^2)]]^{1/2}.$$

Table 3. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms of 1

atom	x	y	z	U(eq), Å ²
La	0.42543(2)	0.47417(1)	0.04566(1)	0.0158(1)
N(1)	0.2383(3)	0.6150(2)	0.0994(2)	0.0222(10)
N(2)	0.6464(3)	0.4984(2)	-0.0783(2)	0.0203(9)
C(1)	0.3742(4)	0.5973(2)	-0.0663(2)	0.0189(11)
C(2)	0.2586(4)	0.6613(2)	-0.0556(3)	0.0199(11)
C(3)	0.2346(4)	0.7309(3)	-0.1144(3)	0.0238(11)
C(4)	0.3242(4)	0.7372(3)	-0.1880(3)	0.0253(12)
C(5)	0.4371(5)	0.6743(2)	-0.2027(2)	0.0234(11)
C(6)	0.4608(4)	0.6054(2)	-0.1421(2)	0.0191(10)
C(7)	0.1540(4)	0.6464(3)	0.0215(2)	0.0246(11)
C(8)	0.3240(5)	0.6925(3)	0.1335(3)	0.0303(12)
C(9)	0.1330(4)	0.5844(3)	0.1671(3)	0.0317(12)
C(10)	0.5751(4)	0.5325(3)	-0.1598(2)	0.0237(10)
C(11)	0.7262(5)	0.4123(3)	-0.0976(3)	0.0320(12)
C(12)	0.7559(4)	0.5662(3)	-0.0481(3)	0.0280(11)
C(13)	0.6581(5)	0.5137(3)	0.1679(3)	0.0340(14)
C(14)	0.5278(5)	0.5066(3)	0.2198(3)	0.0380(16)
C(15)	0.4863(5)	0.4164(4)	0.2238(3)	0.0467(16)
C(16)	0.5877(6)	0.3664(3)	0.1749(3)	0.0463(16)
C(17)	0.6930(5)	0.4258(3)	0.1400(3)	0.0360(14)
C(18)	0.2383(5)	0.3234(3)	0.0575(3)	0.0380(16)
C(19)	0.3462(5)	0.2987(3)	-0.0061(3)	0.0360(14)
C(20)	0.3164(6)	0.3474(3)	-0.0782(3)	0.0450(17)
C(21)	0.1932(6)	0.4023(3)	-0.0648(4)	0.0510(19)
C(22)	0.1438(5)	0.3870(3)	0.0195(4)	0.051(2)

$$^a U(\text{eq}) = 1/3 \text{ of the trace of the orthogonalized } \mathbf{U}.$$

Bruker AC200 instrument. EI-MS spectra (70 eV) were recorded using the direct inlet probe of a Unicam GC-MS Automass spectrometer.

(C₅H₅)₃La·THF.⁹ To a stirred suspension of LaCl₃ (8.75 g; 35.67 mmol) in 50 mL of THF was added a solution of (C₅H₅)₂Na (9.42 g; 107.00 mmol) in 150 mL of THF dropwise at room temperature. The resulting mixture was heated at reflux temperature overnight. After centrifugation of the reaction mixture and subsequent extraction of the residue with hot THF (6 × 75 mL), the combined THF extracts were evaporated and the residue was dissolved in 250 mL of hot THF. Allowing this clear solution to cool to room temperature afforded the crystalline product in 65% yield.

¹H-NMR data (THF-*d*₆, 200 MHz, 298 K): δ 5.95 (s, C₅H₅). ¹³C-NMR data (THF-*d*₆, 50 MHz, 297 K): δ 112.84 (C₅H₅). MS-EI (*m/e* (relative intensity)): 334, (C₅H₅)₃La⁺ (0.6%); 269, (C₅H₅)₂La⁺ (80.3%); 204, (C₅H₅)La⁺ (49.3%); 66, C₅H₆⁺ (100%); 65, C₅H₅⁺ (97.2%). Analysis for sodium: 0%.

(C₅H₅)₂La(C₆H₃{CH₂NMe₂}₂-2,6) (1). To stirred suspension of Cp₃La·THF (2.26 g; 5.56 mmol) in benzene (25 mL) was added a solution of (C₆H₃{CH₂NMe₂}₂-2,6)Li (1.10 g; 5.56 mmol) in benzene (20 mL) dropwise at room temperature. The mixture was heated at reflux temperature overnight and centrifuged. Evaporation of the solvent gave the product as a white powder (2.23 g; 87%).

¹H-NMR data for 1 (C₆D₆, 200 MHz, 297 K): δ 7.11 (m, 1 H, *p*-ArH), 6.88 (m, 2 H, *m*-ArH), 6.08 (s, 10 H, C₅H₅), 3.36 (s, CH₂NMe₂), 2.01 (s, 12 H, CH₂NMe₂). ¹³C-NMR data for 1 (C₆D₆, 50 MHz, 297 K): δ 147.81, 125.49, 121.65(Ar); δ 112.58 (C₅H₅); δ 71.61 (CH₂NMe₂); 47.15 (CH₂NMe₂). Anal. Calcd for C₂₂H₂₉N₂La: C, 57.40; H, 6.35; N, 6.08. Found: C, 57.35; H, 6.43; N, 5.96.

X-ray Data Collection and Structure Refinement. A yellowish crystal of 1 (0.13 × 0.50 × 0.50 mm) was glued on top of a glass fiber and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4T rotating anode diffractometer, using graphite-monochromated Mo K α radiation, for data collection. Accurate unit-cell parameters were determined by least-squares treatment of 25 well-centered reflections (SET4) in the range 11 < θ < 14°. All data (total 4978; unique 4307) were collected in the $\omega/2\theta$ scan mode ($\Delta\omega$, deg = 0.61 + 0.35 tan θ ; data set (*hkl*) 0 to 11, -18 to 19, 0 to 19). Selected crystal data and details on data collection and refinement are collected in Table 2, and final refined atomic coordinates, in Table 3. Selected bond distances and angles are collected in Table 1. Data were corrected for *Lp* effects, for a small linear decay (3%) of the reference reflections, and for absorption (DIFABS;¹³ correction range 0.875–1.234). The structure was solved by Patterson (SHELXS)¹⁴ and subsequent difference Fourier techniques. Refinement was carried out by full-matrix least-squares techniques on *F* (SHELXL76).¹⁵ Hydrogen atoms were introduced on calculated positions and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with four isotropic thermal parameters (aryl, benzylic, methyl, and cyclopentadienyl). Weights were introduced in the last refinement cycles. No residual density was observed in a final difference map outside the range -1.06 < $\Delta\rho$ < 1.04 e/Å³. Neutral atom scattering factors were taken from Cromer and Mann¹⁶ and corrected for anomalous dispersion.¹⁷ All calculations were carried out on a DECstation 5000 cluster. Geometrical calculations and ORTEP drawings were done with PLATON.¹⁸ The final *R*-value of the alternative absolute structure is 0.031.

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Supporting Information Available: Full details of the X-ray structure of complex 1, including tables of hydrogen coordinates and *U* values, bond lengths, bond angles, anisotropic parameters, and data collection parameters (12 pages). Ordering information is given on any current masthead page.

OM950650P

(13) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A* **1983**, *39*, 158.
(14) Sheldrick, G. M. *SHELXS86. Program for crystal structure determination*; University of Göttingen: Göttingen, Federal Republic of Germany, 1986.

(15) Sheldrick, G. M. *SHELXL76. Crystal Structure Analysis Package*; University of Cambridge: Cambridge, England, 1993.

(16) Cromer, D. T.; Mann, J. B. *Acta Crystallogr. Sect. A* **1968**, *24*, 321.

(17) Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891.

(18) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.