Organometallics **2003,** *22,* 2531−2534

Rhodium-Induced Fragmentation and Rearrangement of 4,7,10-Trithiatrideca-2,11-diyne

Lorraine M. Caldwell, Alison J. Edwards, Anthony F. Hill,* Horst Neumann, and
Madeleine Schultz

*Research School of Chemistry, Institute of Advanced Studies, Australian National University,
Canberra, A.C.T. 0200, Australia*

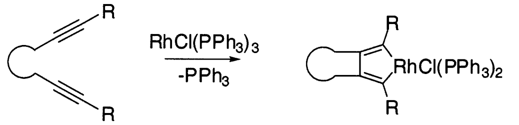
Received January 21, 2003

Summary: The reaction of 4,7,10-trithiatrideca-2,11-diyne with $RhCl(PPh_3)_3$ results in cleavage and rearrangement of the diyne with formation of the structurally characterized complex $RhCl(C{\equiv}CMe)(PPh_3)\{\kappa^3\text{-}S,S',S''\text{-}S(CH{=}CH_2)CH_2CH_2SCH{=}CMeS\}$.

Introduction

Wilkinson's complex, $RhCl(PPh_3)_3$, is known to couple α,ω-diynes to form rhodacyclopentadienes (Scheme 1).[1−3] Metallacyclopentadiene derivatives of many transition metals have been employed as versatile synthetic intermediates.[4] Synthetic protocols based on zirconium[5−7] and cobalt[8−11] have been particularly widely applied. While isolable cobaltacyclopentadienes have been less studied than their group 4 metallocene analogues, their intermediacy in synthetic protocols for the oligomerization of alkynes[10,12,13] and co-oligomerization of alkynes with nitriles[14] is undisputed. Similarly, synthetic routes to cyclobutadiene complexes of cobalt generally proceed via cobaltacyclopentadienes.[15] Although rhodacyclopentadienes have attracted less interest due to the expense of their incorporation in stoichiometric protocols, their synthetic utility has been demonstrated.[3,16−18] We are currently investigating the organometallic chemistry of 4,7,10-trithiatrideca-2,11-diyne (TTDD) with a view to developing synthetic strategies for the formation of macrocyclic thioethers. Accordingly, a rhodacyclopentadiene derived from TTDD appeared an attractive target. Herein we report the reaction of $RhCl(PPh_3)_3$ with TTDD, which, contrary to expectation, does not lead to a rhodacyclopentadiene, but rather proceeds via a complex mechanism involving alkyne cleavage and rearrangement to provide $RhCl(C{\equiv}CMe)(PPh_3)\{\kappa^3\text{-}S,S',S''\text{-}S(CH{=}CH_2)CH_2CH_2SCH{=}CMeS\}$ as the major product.

Scheme 1. General Representation of the Coupling of Diynes by Wilkinson's Complex to Form Rhodacyclopentadienes



Results and Discussion

Heating $RhCl(PPh_3)_3$ with 1 equiv of 4,7,10-trithiatrideca-2,11-diyne (TTDD) under reflux in benzene leads to the formation of an orange solution, from which the major product of the reaction may be isolated and purified by chromatography. The mass spectrum and elemental analysis suggest a composition of "$RhCl(PPh_3)(TTDD)$"; however, the NMR data are inconsistent with the formation of either a simple 1:1 adduct or a rhodacyclopentadiene. To elucidate the structure, the product was characterized crystallographically. Two crystalline materials were obtained under different crystallization conditions, one being the pure complex and the other a dichloromethane monosolvate. No chemically significant differences were noted between the rhodium complexes in the two studies, and so the former will be discussed (details of the latter are included in the Supporting Information).

The molecular structure of the product $RhCl(C{\equiv}CMe)(PPh_3)\{\kappa^3\text{-}S,S',S''\text{-}S(CH{=}CH_2)CH_2CH_2SCH{=}CMeS\}$ (**1**), shown in Figure 1, contains a pseudo-octahedral environment about rhodium(III), which retains a chloride ligand and one triphenylphosphine. The features of note are (i) a propynyl ligand and (ii) a novel tridentate bis(thioether)thiolate ligand. The alkynyl ligand is unremarkable, with conventional Rh−C and C≡C separations (2.014(5) and 1.181(6) Å, respectively). The organosulfur ligand is facially coordinated through two thioether donors (Rh−S1 = 2.398(1) Å and

---

* Corresponding author. E-mail: a.hill@rsc.anu.edu.au.

(1) Müller, E. *Synthesis* **1974**, *11*, 761−774.

(2) Müller, E.; Winter, W. *Justus Liebigs Ann. Chem.* **1974**, 1876−1881.

(3) Scheller, A.; Winter, W.; Müller, E. *Justus Liebigs Ann. Chem.* **1976**, 1448−1454.

(4) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119.

(5) Takahashi, T.; Kotora, M.; Hara, R.; Xi, Z. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2591−2602.

(6) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696−1701.

(7) Negishi, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, UK, 1991.

(8) Catellani, M.; Chiusoli, G. P.; Costa, M. *J. Organomet. Chem.* **1995**, *500*, 69−80.

(9) Zhou, Z.; Costa, M.; Chiusoli, G. P. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1399−1406.

(10) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539−556.

(11) Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1978**, 1278−1282.

(12) Diercks, R.; Eaton, B. E.; Guertzen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247−8248.

(13) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295−311.

(14) Bönnemann, H.; Brijoux, W. *Adv. Heterocycl. Chem.* **1990**, *48*, 177−222.

(15) Efraty, A. *Chem. Rev.* **1977**, *77*, 691−744.

(16) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Vacca, A.; Laschi, F.; Zanello, P. *Organometallics* **1991**, *10*, 636−645.

(17) Müller, J.; Akhnoukh, T.; Gaede, P. E.; Guo, A.-L.; Moran, P.; Qiao, K. *J. Organomet. Chem.* **1997**, *541*, 207−217.

(18) Rourke, J. P.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Chem. Commun.* **2001**, 2626−2627.

10.1021/om030040m CCC: $25.00
Publication on Web 05/13/2003

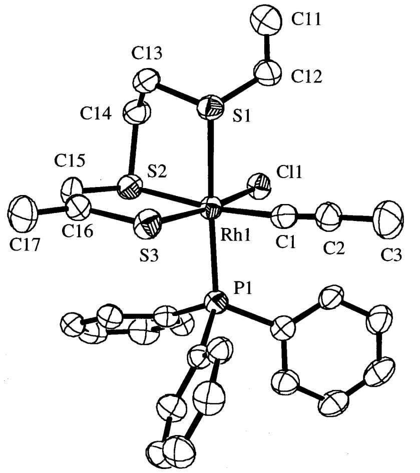
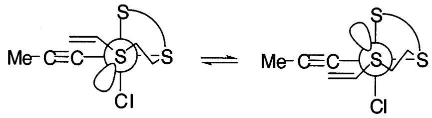


Figure 1. ORTEP diagram (50% probability displacement ellipsoids) of compound **1** showing atom-numbering scheme. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg): Rh−S1 2.398(1); Rh−S2 2.367(1); Rh−S3 2.316(1); Rh−C1 2.014(5); C1−C2 1.181(6); C2−C3 1.481(7); C11−C12 1.317(7); C15−C16 1.328(7); C13−C14 1.510(6); Rh−C1−C2 174.3(4); C1−C2−C3 177.2(5).

Scheme 2. Schematic Representation of the Interconversion of the Two Diastereomers of 1 through Inversion at S1, Depicted Viewed along the S1−Rh Axis



Rh−S2 = 2.367(1) Å) and one thiolato group (Rh−S3 = 2.316(1) Å), and, in each case, the Rh−S separation is consistent with norms for thiolate and thioether coordination to rhodium(III).[19−21] The chemically curious aspect of this ligand is, however, the propenyl linkage between S2 and S3. This metallacycle is essentially planar, with the olefinic bond (C15−C16 = 1.328(7) Å) being somewhat long, as expected for an alkene bearing conjugated π-dative substituents.

With the structure in hand, the spectroscopic data were revisited. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra are complex for reasons detailed for the simplest case, ^{31}P{^{1}H}. At room temperature in CD_2Cl_2, this spectrum comprises a broadened four-line pattern around δ 35.5 ($\nu_{1/2}$ = 40 Hz), which, at first glance, appears inconsistent with a monophosphine complex of rhodium. However, the molecular structure includes chiral sulfur centers (S1 and S2), and the rhodium center itself has six disparate donor groups. Thus, diastereomers may arise that might in principle be interconverted by inversion at S1 (Scheme 2). This appears to be the case, as demonstrated by comparison of the ^{31}P{^{1}H} NMR spectra at different temperatures and in different solvents. In 1,1,2,2-tetrachloroethane-d_2 at −35 °C, two sharp doublets are observed at δ 33.7 ($^{1}J_{PRh}$ = 120, $\nu_{1/2}$ = 9 Hz) and 33.5 ($^{1}J_{PRh}$ = 120, $\nu_{1/2}$ = 6 Hz) in an integrated ratio of 1:1.3. At +25 °C and above, a single doublet is observed at δ 33.6; at +65 °C this is sharp ($^{1}J_{PRh}$ = 120, $\nu_{1/2}$ = 4 Hz). A stacked plot of the ^{31}P{^{1}H} spectra over this temperature range is shown in Figure 2. The coalescence temperature of 0 °C corresponds to an activation barrier for sulfur inversion of 44(3) kJ/mol.[22] Similar changes were seen in the ^{31}P{^{1}H} spectra in CD_2Cl_2, but at the highest measurable temperature in that solvent (+40 °C), the doublet remained broad ($\nu_{1/2}$ = 38 Hz); that is, the fast exchange regime had not been reached. The coalescence temperature in CD_2Cl_2 of +30 °C corresponds to an activation barrier of 63(3) kJ/mol, with the relative population of the two isomers being the same as in $CDCl_2CDCl_2$ (1:1.3). The sample in CD_2Cl_2 was cooled further, and at −60 °C a further decoalescence of the ^{31}P{^{1}H} resonances was observed, with the new resonances becoming sharper at −80 °C. A stacked plot of the ^{31}P{^{1}H} spectra in CD_2Cl_2 (−80 to +40 °C) is provided as Supporting Information.

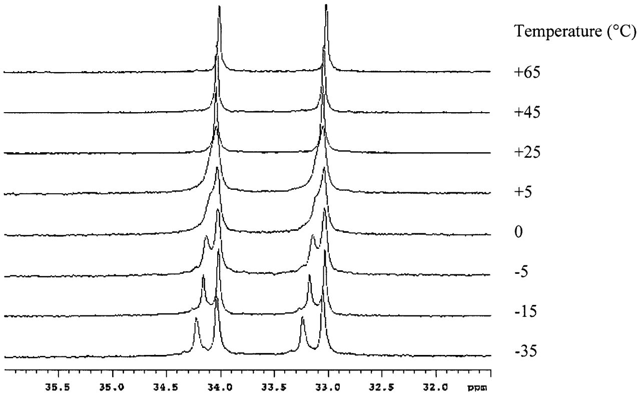


Figure 2. Stacked plot of ^{31}P{^{1}H} NMR spectra of **1** in $CDCl_2CDCl_2$.

Inversion of nonsymmetric thioether complexes is well documented,[23] and the barriers found for **1** are within the normal range for a thioether coordinated to a transition metal, despite the inclusion of the inverting group within a bicyclic bis-chelate structure. The increase in inversion barrier moving from the less polar $CDCl_2CDCl_2$ to the more polar CD_2Cl_2 indicates that the energy difference between each diastereomer and the transition state increases in a more polar medium. This is thought to arise from the loss of C−D···S solvation of the sulfur lone pair (greater in a more polar solvent) on approach to a transition state involving trigonally coordinated sulfur. Both diastereomers would be expected to have similar solvation energies, so the equal ratios of diastereomer populations in the two solvents is not surprising. The temperature dependence of the spectra is also consistent with thioether dissociation and recoordination; however, in that case a polar solvent might be expected to decrease the activation barrier by solvation of charge development in the (unsaturated) intermediate. Simple δ/λ inversion of the $RhSCH_2CH_2S$ metallacycle is likely to be a low-energy process, which is, in any event, likely to occur in tandem with sulfur inversion.

---

[19] Binger, P.; Biedenback, B.; Mynott, R.; Krüger, C.; Betz, P.; Regitz, M. *Angew. Chem.* **1988**, *100*, 1219−1221.

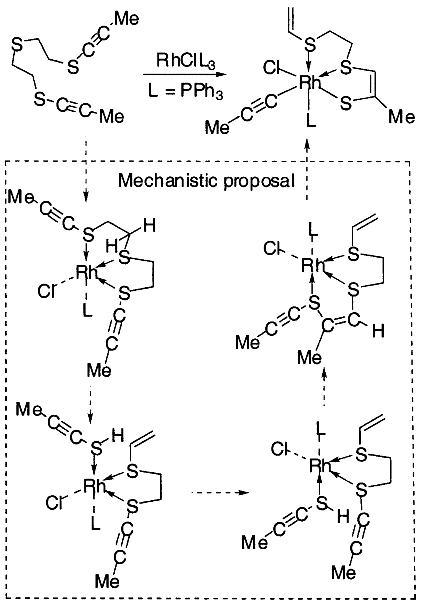
[20] Blake, A. J.; Holder, A. J.; Hyde, T. I.; Kuppers, H.-J.; Schröder, M.; Stötzel, S.; Wieghardt, K. *J. Chem. Soc., Chem. Commun.* **1989**, 1600−1602.

[21] Blake, A. J.; Halcrow, M. A.; Schröder, M. *Acta Crystallogr. C* **1993**, *49*, 85−87.

[22] Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

[23] Abel, E. W.; Bhargava, S. K.; Orrell, K. G. *Prog. Inorg. Chem.* **1984**, *32*, 1−118.

Scheme 3. Proposed Mechanism for the Formation of 1



The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are also complicated by the fluxional behavior of the complex. At −35 °C in $CDCl_2CDCl_2$, the α-vinylic protons from the two diastereomers are manifest as a six-line pattern comprising two overlapping doublets of doublets at δ 6.75. At +65 °C (fast exchange regime), this is collapsed to one doublet of doublets at δ 6.77, and the coupling constants to the adjacent *cis*- and *trans*-vinylic β-hydrogens can be observed ($^{3}J_{HHcis} = 10$ Hz, $^{3}J_{HHtrans} = 17$ Hz). Similarly, the terminal vinylic CH_2 resonances simplify from a multiplet at −35 °C, to two doublets (δ 5.97 and 5.83) showing typical *cis*- and *trans*-couplings to the α-vinylic proton ($^{3}J_{HHcis} = 10$ Hz, $^{3}J_{HHtrans} = 17$ Hz) on warming to +65 °C. The proton of the propenyl linkage appears as two broadened doublets at −35 °C, collapsing to a singlet (δ 4.52) at +65 °C, while the broad peaks of the ethylene bridge become sharper at higher temperatures. Each methyl group of the complex gives rise to two resonances at low temperature for the two diastereomers, which coalesce to singlets upon warming. A stacked plot of these spectra is included in the Supporting Information. Similar behavior is observed in CD_2Cl_2 (a stacked plot is included in the Supporting Information) and also for the $^{13}C\{^{1}H\}$ spectra. The HMQC (C−H correlation) spectra of **1** in CD_2Cl_2 at 25 and −20 °C are included in the Supporting Information.

The mechanism by which **1** forms remains obscure but clearly involves multiple steps involving C−S bond cleavage and formation. At present, we have no evidence for a mechanism; however, a tentative proposal is provided in Scheme 3. That complex **1** is the only organorhodium product observed suggests that the mechanistic manifold involves intramolecular transformations after coordination of TTDD. We have recently structurally characterized a simple κ^{3}-S,S',S'' adduct of TTDD with $AgPF_6$,[24] providing precedent for the proposed initial coordination. The co-ligands in this and subsequent intermediates are open to debate, with either "$RhCl(PPh_3)$" or "$Rh(PPh_3)_2^{+}$" acting as a template. The tridentate thioether 1,4,7-trithiacyclonane ([9]aneS_3) reacts with $RhCl(PPh_3)_3$ followed by anion exchange to provide the cationic complex $[Rh(PPh_3)_2([9]aneS_3)]^{+}[PF_6]^{-}$.[25] However, the use of nonpolar arene solvents in the present study makes neutral intermediates based on the "$RhCl(PPh_3)$" fragment more likely. The 1,2-elimination of coordinated propynyl mercaptan could install the vinylic thioether group. This second step would represent the microscopic reverse of the metal-catalyzed addition of thiols to alkenes, for which there is some precedent.[26] In a subsequent step, we envisage addition of the propynylmercaptan S−H bond to the pendant propynyl thioether linkage to install the chelated propenyl linkage. Again, there exists limited precedent for the metal-catalyzed addition of thiols to alkynes.[26] The final step might then involve oxidative addition of the remaining alkynyl thioether linkage to provide the final product, **1**. Many alternative mechanisms can also be conceived. In particular, metal hydrides are potential intermediates in hydrogen transfer steps, although a coordinatively saturated metal hydride would be incapable of adding across the alkyne with the observed olefinic cis-β regiochemistry. In any event, the manifold of transformations required to convert TTDD to the final product are remarkable and point toward a diverse organometallic chemistry for this α,ω-diyne. Attempts to observe intermediates in the formation of **1** by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy were unsuccessful; only unreacted TTDD and free PPh_3 were observed before heating; upon heating, **1** was also observed.

The reaction of **1** with an acid might be expected to result in cyclization of the pendant vinyl group with the thiolate to form an unsaturated [9]eneS_3 derivative, as reversible base-induced cleavage of [9]aneS_3 has been reported on transition metals including rhodium.[20,27] However, no tractable products were formed in the reaction of **1** with aqueous HPF_6; the base-induced cleavage of [9]aneS_3 has also been found to be irreversible on rhodium.[28]

Experimental Section

A mixture of $RhCl(PPh_3)_3$ (0.50 g, 0.54 mmol) and 4,7,10-trithiatrideca-2,11-diyne[24] (0.12 g, 0.54 mmol) in benzene (60 mL) was heated at reflux under nitrogen for 1 h. The resulting orange-brown solution was transferred to a short silica column, and the liberated triphenylphosphine was eluted with benzene. The orange band was then eluted with dichloromethane and taken to dryness under dynamic vacuum. The residue was then recrystallized from a 40:60 benzene/hexane mixture. Yield after purification: 0.17 g of orange powder (50%), mp 170−172 °C (dec) Anal. Found: C, 53.38; H, 4.66; P, 4.80; S, 14.91. Calcd for $C_{28}H_{29}RhPClS_3$: C, 53.29; H, 4.63; P, 4.91; S, 15.24. ^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 7.98 (m, 6 H, C_6H_5), 7.35 (m, 9 H, C_6H_5), 6.68 (m(br), 1 H, SC*H*=CH_2), 5.82 (m(br), 2 H, SCH=CH_2), 4.55 (s(br), 1 H, SC*H*CMe), 2.5−3.2 (m(br), 4 H, SCH_2CH_2S), 2.07 (s, 3 H, C≡CCH_3), 1.91 (s, 3 H, $SCCH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_2CDCl_2$, 298 K, 75 MHz): δ 171.2 (S*C*Me, C16), 136.3 (d, $^{3}J_{PC} = 9.0$ Hz, $C^{3,5}(C_6H_5)$), 133.3 (Rh*C*≡C, C1),

---

[24] Edwards, A. J.; Hill, A. F.; Neumann, H.; Niess, B. Manuscript in preparation.

[25] Hill, A. F.; Wilton-Ely, J. D. E. T. *Organometallics* **1997**, *16*, 4517−4518.

[26] Ogawa, A. *J. Organomet. Chem.* **2000**, *611*, 463−474.

[27] Bennett, M. A.; Goh, L. Y.; Willis, A. C. *J. Am. Chem. Soc.* **1996**, *118*, 4984−4992.

[28] Brandt, K.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1996**, 1237−1243.

133.3 (d, $^{1}J_{PC} = 53.3$ Hz, $C^{1}(C_6H_5)$,), 130.2 (d, $^{2}J_{RhC} = 12.1$ Hz, S*C*H=CH$_2$, C12), 129.3 (d, $^{4}J_{PC} = 10.0$ Hz, $C^{4}(C_6H_5)$), 129.1 (d, $^{2}J_{PC} = 11.1$ Hz, $C^{2,6}(C_6H_5)$), 124.2 (br, SCH=*C*H$_2$, C11), 103.2 (RhC≡*C*, C2), 101.5 (S*C*H=CMe, C15), 41.0 (br, SCH$_2$), 37.4 (br, SCH$_2$), 24.3 (SC*C*H$_3$, C17), 8.50 (C≡C*C*H$_3$, C3). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 298 K, 121 MHz): δ 34.7 (d, $^{1}J_{PRh} = 120$ Hz, $\nu_{1/2} = 38$ Hz), 34.2 (d, $^{1}J_{PRh} = 120$ Hz, $\nu_{1/2} = 38$ Hz). IR Nujol: 2140 ($\nu_{C\equiv C}$), 1596, 1546 ($\nu_{C=C}$) cm^{-1}. CH$_2$Cl$_2$: 2144 ($\nu_{C\equiv C}$), 1597, 1553 ($\nu_{C=C}$) cm^{-1}. MS (APCI+): 668.9 [M + Na + O], 652.9 [M + Na], 630.8 [M + H], 611.0 [M + O − Cl], 595.0 [M − Cl], 554.9 [M − CCCH$_3$ − Cl − H] (isotopic distributions confirmed by simulation).

X-ray Crystallography. Data were collected on a Nonius KappaCCD diffractometer.[29] The structure was solved by direct methods[30] and refined via a full matrix least squares procedure against *F*.[31]

Crystal data for 1: $C_{28}H_{29}ClPRhS_3$, $M = 631.05$, monoclinic, $P2_1/a$ (#14), $a = 17.7575(4)$ Å, $b = 9.1244(3)$ Å, $c = 18.9470(5)$ Å, $\beta = 116.484(1)°$, $V = 2747.0(5)$ Å^3, $Z = 4$, $\rho_{calc} = 1.526$ g cm^{-3}, μ(Mo Kα) = 1.02 mm^{-1}, $T = 200$ K, yellow plate, 6269 independent measured reflections, $R_1 = 0.027$, $wR_2 = 0.027$, 2637 independent observed absorption-corrected reflections [$I > 3\sigma(I)$, $2\theta \leq 54.9°$], 307 parameters.

Supporting Information Available: Tables giving crystallographic details for **1** and **1**·CH$_2$Cl$_2$; stacked plots of NMR spectra of **1** in CDCl$_2$CDCl$_2$ (−35 to +65 °C) (^{31}P{^{1}H} and ^{1}H) and in CD$_2$Cl$_2$ (−80 to +40 °C) (^{31}P{^{1}H} and ^{1}H); HMQC (C−H correlation) spectra of **1** in CD$_2$Cl$_2$ at 25 and −20 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030040M

---

(29) *COLLECT programme suite*; Nonius BV, 1997−2001.

(30) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(31) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W.; Cooper, R. I. *CRYSTALS programme suite*; Chemical Crystallography Laboratory: Oxford, 2001.