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The first trialkylphosphane telluride complexes of Ag(I): molecular, ionic and supramolecular structural alternatives

Constantin Daniliuc, Christian Druckenbrodt, Cristian G. Hrib, Frank Ruthe, Armand Blaschette, Peter G. Jones and Wolf-W. du Mont*

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The structures of the first phosphane telluride complexes of silver(I), obtained from *i*-Pr_3PTe (1) with $AgNMs_2$ [Ms = SO_2CH_3] and with $AgSbF_6$, reveal the superior coordinating ability of 1, particularly as a bridging ligand, compared with related *i*-Pr_3PS and *i*-Pr_3PSe ligands.

In view of the softness of tellurium and of the dipolar character of the $P^+–Te^-$ bond, phosphane tellurides R_3PTe should act towards soft metal ions as ligands that are superior to the well-established phosphane oxides, sulfides and selenides. There are, however, only a few trialkylphosphane telluride complexes known, and *t*-$Bu_3PTeW(CO)_5$ is the only one to be structurally characterized.[1] The tendency of R_3PTe to decompose in the presence of Lewis acids (by detelluration)[2] and their kinetic lability in the presence of free phosphanes (reversible Te transfer)[3] has led to their use as carriers of zero valent tellurium,[4] for instance in the formation of semiconductor materials[5] or metal polytelluride ions such as $[AgTe_7]^{3-}$.[6] In the latter case, however, the role of phosphane telluride silver complexes was not recognized. Anionic bidentate phosphane tellurides are less susceptible to detelluration than uncharged phosphane tellurides,[7] and coinage metal complexes with $\{[R_2P(Te)]_2N\}^-$ ligands (R = *i*-Pr, Ph) were very recently reported by Chivers *et al.* at a scientific meeting.[8]

Our study on coinage metal chloride interactions with trialkylphosphane tellurides revealed that CuCl complexes with *i*-Pr_3PTe (**1**) and with *t*-Bu_3PTe are short-lived species that can be detected using ^{31}P-NMR spectroscopy before they decompose by loss of tellurium, giving the stable complexes R_3PCuCl, whereas with the tetrahydrothiophene–AuCl complex, immediate precipitation of tellurium after addition of **1** leads to *i*-Pr_3PAuCl.[9]

The complex *t*-$Bu_3PTeAgCl$ also decomposes within a short time, leading to *t*-Bu_3PAgCl, but with *i*-Pr_3PTe (**1**), after separation from a black residue, a solid yellow 1 : 1 complex can be characterized using elemental analyses and ^{31}P-NMR spectroscopy, exhibiting $^1J(^{125}Te, ^{31}P)$ satellites with magnitudes about 15% smaller than those of the free ligand.[9]

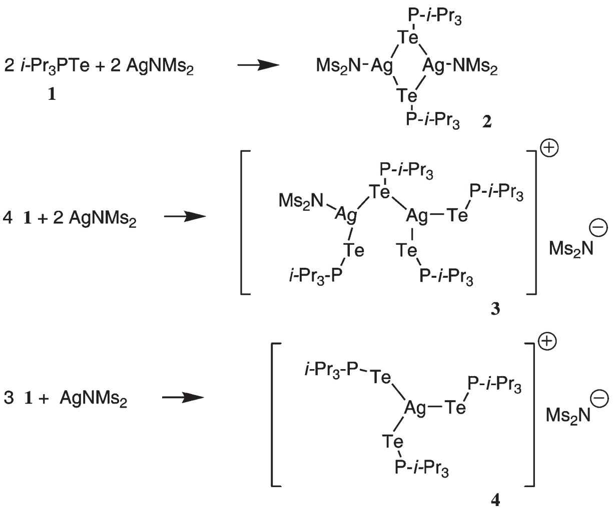
$$i\text{-}Pr_3PTe + CuCl \longrightarrow \{i\text{-}Pr_3PTeCuCl\} \longrightarrow i\text{-}Pr_3PCuCl + Te$$

$$t\text{-}Bu_3PTe + AgCl \longrightarrow \{t\text{-}Bu_3PTeAgCl\} \longrightarrow t\text{-}Bu_3PAgCl + Te$$

$$i\text{-}Pr_3PTe + AgCl \longrightarrow i\text{-}Pr_3PTeAgCl$$

$$i\text{-}Pr_3PTe + THT\text{-}AuCl \longrightarrow i\text{-}Pr_3PAuCl + Te + THT$$

Our unsuccessful attempts to grow single crystals of *i*-$Pr_3PTeAgCl$ and *i*-$Pr_3PTeAgBr$ led us to use silver(I)–di(methylsulfonyl)amide $[AgNMs_2]$[10] as an alternative substrate for *i*-Pr_3PTe. By mixing the appropriate amounts of **1** with $AgNMs_2$ in acetonitrile, a set of stable 1 : 1, 2 : 1 and 3 : 1 phosphane telluride silver complexes **2** (1 : 1), **3** (2 : 1) and **4** (3 : 1) became available.†



2

3

4

^{31}P-NMR spectra of **2–4** and of mixtures of **2–4** with ligand **1** in CH_3CN or in CH_2Cl_2 solution show averaged singlet signals with satellites from $^1J(^{125}Te, ^{31}P)$ coupling; splitting by coupling with ^{107,109}Ag does not occur. Consistent with the kinetic lability of all complexes with respect to Te–Ag coordination, whereby rapid Te–P bond breaking does not occur, the ^{125}Te-NMR spectra of **2–4** exhibit doublet signals, the magnitudes of $^1J(^{125}Te, ^{31}P)$ coupling following the order **2** < **3** < **4** < **1**.

Complexes **2–4** were studied by single crystal X-ray diffraction.‡ The 1 : 1 complex **2** (Fig. 1) is an inversion-symmetric molecular dimer with bridging tellurium atoms from the two *i*-Pr_3PTe ligands; each Ag atom is also N-coordinated by a NMs_2^- anion (planar Ag, CN 3).[9] Compared with the related *i*-Pr_3PS and *i*-Pr_3PSe complexes,[11] **2** exhibits shorter Ag···Ag contacts (by about 0.18 Å) and slightly longer Ag–N bonds.

The overall formula of the 2 : 1 complex **3** (Fig. 2) is that of an unsymmetric dimer that contains one terminally N-coordinated and one uncoordinated NMs_2^- anion. In the dinuclear cation, *one* *i*-Pr_3PTe bridges the two Ag atoms; Ag1 is 3-coordinated by the bridging and two terminal *i*-Pr_3PTe ligands, and Ag2 is 3-coordinated by the NMs_2^- anion, the bridging and one terminal *i*-Pr_3PTe ligands. This structure is very different from that of the

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Institut für Anorg. u. Analyt. Chemie der Technischen Universität Braunschweig, Postfach 3329, D 38023 Braunschweig, Germany. E-mail: w.du-mont@tu-bs.de

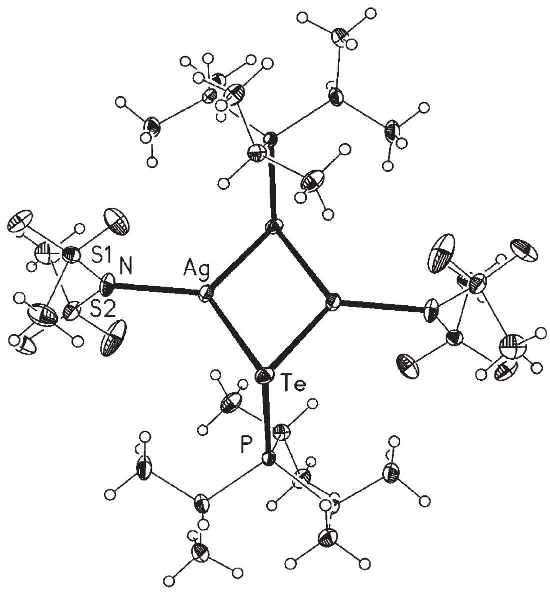

Fig. 1 Molecular structure of $[Ag_2(NMs_2)_2(i\text{-}Pr_3PTe)_2]$ (**2**). Selected distances (Å): Ag–Te 2.8117(6); Ag–Te#1 2.8024(6); Ag–N 2.258(3); Ag···Ag#1 2.9075(7).

related *i*-Pr_3PS 2 : 1 complex which crystallizes as a simple monomer with terminal *i*-Pr_3PS and NMs_2^- ligands.[11]

The 3 : 1 complex **4** consists of Ag^+ cations surrounded by three terminal *i*-Pr_3PTe ligands in a regular trigonal geometry;[11] this ionic structure with separated NMs_2^- anions is closely related to those of the corresponding *i*-Pr_3PS and *i*-Pr_3PSe complexes.[11] However, the structure of **4** and of its SbF_6 analogue are affected by disorder or twinning phenomena and the refinements are unsatisfactory. The P–Te bond distances in **2–4** are between 2.40 and 2.43 Å (**1**: 236.8 pm);[1] significant differences between terminal and bridging ligands are not observed.

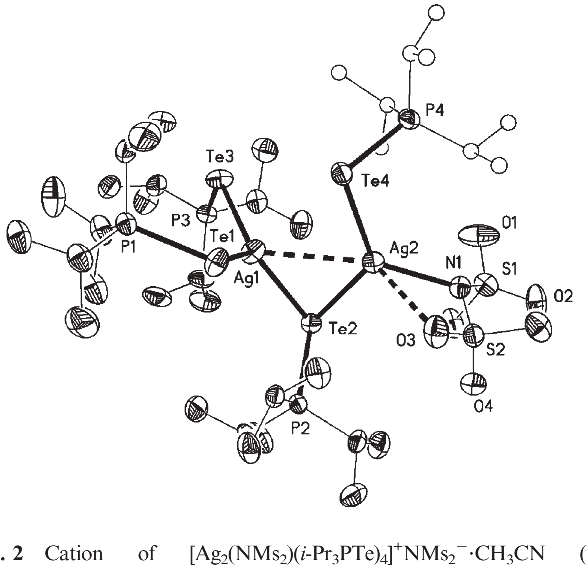

Fig. 2 Cation of $[Ag_2(NMs_2)(i\text{-}Pr_3PTe)_4]^+NMs_2^-\cdot CH_3CN$ (**3**). Hydrogen atoms, solvent and the uncoordinated NMs_2^- group are omitted for clarity. The isopropyl groups at P4 are disordered over two positions. Selected distances (Å): Ag1–Te1 2.7281(9); Ag1–Te2 2.7638(9); Ag1–Te3 2.7181(9); Ag2–Te2 2.7947(9); Ag2–Te4 2.6956(9); Ag2–N1 2.422(7); Ag2···O3 2.773(6); Ag1···Ag2 3.1437(11).

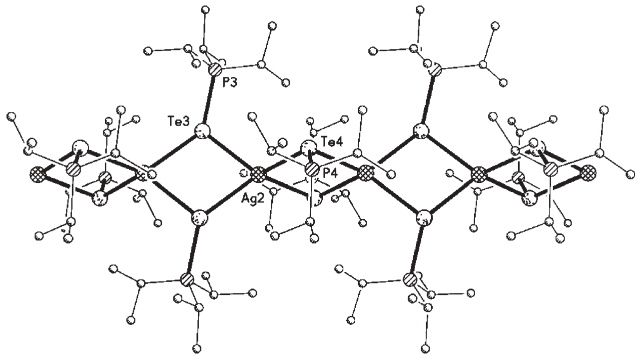

Fig. 3 One of two crystallographically independent cationic chains in $[Ag(i\text{-}Pr_3PTe)_2]SbF_6$ (**5**). Hydrogen atoms are omitted for clarity. Selected distances (Å): chain 1, not shown: Ag1–Te1 2.9359(7); Ag1–Te2 2.8557(7); Ag1–Te#1 2.7857(7); Ag1–Te#2 2.8036(7); chain 2: Ag2–Te3 2.7943(7); Ag2–Te4 2.7692(7); Ag2–Te#3 2.8740(7); Ag2–Te#4 2.9011(7).

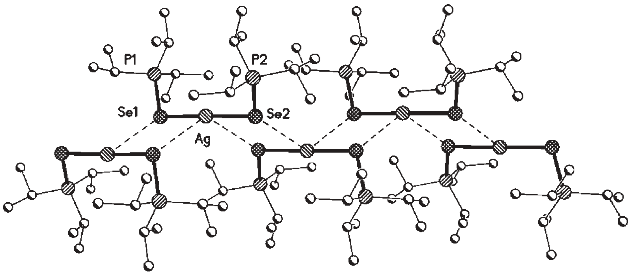

Fig. 4 Weak cation–cation contacts in $[Ag(i\text{-}Pr_3PSe)_2]SbF_6$ (**6**). Hydrogen atoms are omitted for clarity. Selected distances (Å): Ag–Se1 2.5067(3); Ag–Se2 2.4975(3); Ag–Se#1 3.1201(3); Ag–Se#2 3.3206(3).

The structural features of **2** and **3** confirm that the ability of *i*-Pr_3PTe (**1**) to coordinate with Ag^+ (in competition with anionic NMs_2^-) is superior to that of *i*-Pr_3PS and *i*-Pr_3PSe. In the dimeric 1 : 1 complex **2**, coordinating **1** leads to a longer (weaker) Ag–N contact; in the dimeric 2 : 1 complex **3**, coordinating **1** expels one NMs_2^- ligand and the preferred CN 3 of Ag is retained by the bridging role of one the four *i*-Pr_3PTe ligands.

The special role of *i*-Pr_3PTe as a bridging ligand is even more evident in the 2 : 1 complex **5** with $AgSbF_6$ (Fig. 3).

In contrast to the related solid *i*-Pr_3PE complexes (E = S, Se), which are made up from cations $[Ag(i\text{-}Pr_3PE)_2]^+$ (linear E–Ag–E) exhibiting weak "step-like" cation–cation contacts (Fig. 4; **6**: Ag–Se 2.49–2.50 Å; Ag···Se 3.12–3.32 Å),[11] $[Ag(i\text{-}Pr_3PTe)_2]SbF_6$ (**5**) contains a cationic coordination polymer[12] that involves a linear spirocyclic array of centrosymmetric four-membered Ag_2Te_2 rings (Ag–Te 2.769–2.901 Å).

All *i*-Pr_3PTe ligands in **5** are bridging and the Ag^+ ions lie in a distorted tetrahedral environment of four trigonal-pyramidally coordinated Te atoms.

In summary, trialkylphosphane tellurides can act as excellent *soft bridging ligands*, which deserve particular interest beyond their role as sources of tellurium atoms.

Notes and references

† *Selected spectroscopic data*: **2**: Yield 60.4%; found: C, 23.6; H, 4.8; N, 2.4. $C_{11}H_{27}AgNO_4PS_2Te$ requires C, 23.3; H, 4.8; N, 2.5%; MS (FAB[NBA]): *m*/*z* 962 $[\{(i\text{-}Pr_3PTe)_2Ag_2NMs_2\}^+$, 15%], 683 $[\{(i\text{-}Pr_3PTe)_2Ag\}^+$, 88], 557

[{(*i*-Pr$_3$PTe)(*i*-Pr$_3$P)Ag}$^+$, 62], 397 [{(*i*-Pr$_3$PTe)Ag}$^+$, 60], 267 [(*i*-Pr$_3$PAg)$^+$, 100]; δ_H (300.1 MHz; CD$_3$CN; Me$_4$Si) 2.84 (3H, s, SC*H*$_3$), 2.57 (1H, d sept, J_{HH} 7.1, J_{HP} 9.9, C*H*(CH$_3$)$_2$), 1.23 (6H, dd, J_{HH} 7.1, J_{HP} 17.4, CH(C*H*$_3$)$_2$); δ_C (75.4 MHz; CD$_3$CN; Me$_4$Si) 43.02 (s, S*C*H$_3$), 27.73 (d, J_{CP} 28.0, *C*H(CH$_3$)$_2$), 19.79 (d, J_{CP} 2.8, CH(*C*H$_3$)$_2$); δ_P (121.5 MHz; CD$_3$CN; 85%-H$_3$PO$_4$) 48.21 (s, $J_{P\text{-}125\text{-}Te}$ 1418.6, $J_{P\text{-}123\text{-}Te}$ 1176.5, J_{PC} 27.9); δ_{Te} (94.7 MHz; CD$_3$CN; Me$_2$Te) −825.18 (d, J_{TeP} 1419.5).

3: Yield 81.1%; found: C, 28.2; H, 5.9. $C_{20}H_{48}AgNO_4P_2S_2Te_2$ requires C, 28.1; H, 5.7%; MS (FAB[NBA]): *m*/*z* 683 [{(*i*-Pr$_3$PTe)$_2$Ag}$^+$, 100%], 557 [{(*i*-Pr$_3$PTe)(*i*-Pr$_3$P)Ag}$^+$, 30], 397 [{(*i*-Pr$_3$PTe)Ag}$^+$, 42], 267 [(*i*-Pr$_3$PAg)$^+$, 40]; δ_H (300 MHz; CD$_3$CN; Me$_4$Si) 2.75 (3H, s, SC*H*$_3$), 2.3–2.5 (1H, m, C*H*(CH$_3$)$_2$), 1.23 (6H, dd, J_{HH} 7.1, J_{HP} 17.3, CH(C*H*$_3$)$_2$); δ_C (75.4 MHz; CD$_3$CN; Me$_4$Si) 42.67 (s, S*C*H$_3$), 27.20 (d, J_{CP} 28.3, *C*H(CH$_3$)$_2$), 19.74 (d, J_{CP} 1.9, CH(*C*H$_3$)$_2$); δ_P (121.5 MHz; CD$_3$CN; 85%-H$_3$PO$_4$) 47.33 (s, $J_{P\text{-}125\text{-}Te}$ 1451.6, $J_{P\text{-}123\text{-}Te}$ 1204.0, J_{PC} 28.1); δ_{Te} (94.7 MHz; CD$_3$CN; Me$_2$Te) −860.74 (d, J_{TeP} 1451.9).

4: Yield 82%; found: C, 31.3; H, 5.9; N, 1.2; S, 5.2. $C_{29}H_{69}AgNO_4P_3S_2Te_3$ requires C, 30.5; H, 6.0; N, 1.2; S, 5.6%; MS (FAB[NBA]) *m*/*z* 685 [{(*i*-Pr$_3$PTe)$_2$Ag}$^+$, 100%], 557 [{(*i*-Pr$_3$PTe)(*i*-Pr$_3$P)Ag}$^+$, 16], 397 [{(*i*-Pr$_3$PTe)Ag}$^+$, 40], 267 [(*i*-Pr$_3$PAg)$^+$, 30]; δ_H (300 MHz; CD$_3$CN; Me$_4$Si) 2.72 (3H, s, SC*H*$_3$), 2.41 (1H, d sept, C*H*(CH$_3$)$_2$), 1.20 (6H, dd, J_{HH} 7.1, J_{HP} 17.1, CH(C*H*$_3$)$_2$); δ_C (75.4 MHz; CD$_3$CN; Me$_4$Si) 42.62 (s, S*C*H$_3$), 27.20 (d, J_{CP} 28.1, *C*H(CH$_3$)$_2$), 19.72 (d, J_{CP} 2.8, CH(*C*H$_3$)$_2$); δ_P (121.5 MHz; CD$_3$CN; 85%-H$_3$PO$_4$) 45.47 (s, $J_{P\text{-}125\text{-}Te}$ 1498.6, $J_{P\text{-}123\text{-}Te}$ 1246.1, J_{PC} 27.9); δ_{Te} (94.7 MHz; CD$_3$CN; Me$_2$Te) −892.45 (d, J_{TeP} 1501.7).

5: Yield 84.6%; found: C, 23.5; H, 4.6. $C_{18}H_{42}AgF_6P_2SbTe_2$ requires C, 23.7; H, 4.5%; MS (FAB[NBA]) *m*/*z* 683 [{(*i*-Pr$_3$PTe)$_2$Ag}$^+$, 100], 557 [{(*i*-Pr$_3$PTe)(*i*-Pr$_3$P)Ag}$^+$, 12], 397 [{(*i*-Pr$_3$PTe)Ag}$^+$, 35]; δ_H (300 MHz; CD$_3$CN; Me$_4$Si) 2.54 (1H, d sept, J_{HH} 7.1, J_{HP} 9.9, C*H*(CH$_3$)$_2$), 1.28 (6H, dd, J_{HH} 7.1, J_{HP} 16.8, CH(C*H*$_3$)$_2$); δ_C (75.4 MHz; CD$_3$CN; Me$_4$Si) 27.15 (d, J_{CP} 28.8, *C*H(CH$_3$)$_2$), 19.68 (d, J_{CP} 2.8, CH(*C*H$_3$)$_2$); δ_P (121.5 MHz; CD$_3$CN; 85%-H$_3$PO$_4$) 48.20 (s, $J_{P\text{-}125\text{-}Te}$ 1434.8, J_{PC} 28.7); δ_{Te} (94.7 MHz; CD$_3$CN; Me$_2$Te) −848.20 (d, J_{TeP} 1435.6).

6: Yield 91.5%; found: C, 26.3; H, 5.1. $C_{18}H_{42}AgF_6P_2SbSe_2$ requires C, 26.4; H, 5.1%; MS (FAB[NBA]) *m*/*z* 587 [{(*i*-Pr$_3$PSe)$_2$Ag}$^+$, 100], 347 [{(*i*-Pr$_3$PSe)Ag}$^+$, 64]; δ_H (200 MHz; CD$_3$CN; Me$_4$Si) 2.85 (3H, s, SC*H*$_3$), 2.53 (1H, d sept, J_{HH} 7.1, J_{HP} 10.8, C*H*(CH$_3$)$_2$), 1.29 (6H, dd, J_{HH} 7.1, J_{HP} 16.9, CH(C*H*$_3$)$_2$); δ_C (50.2 MHz; CD$_3$CN; Me$_4$Si) 42.64 (s, S*C*H$_3$), 27.63 (d, J_{CP} 36.4, *C*H(CH$_3$)$_2$), 18.34 (d, J_{CP} 2.8, CH(*C*H$_3$)$_2$); δ_P (81.0 MHz; CD$_3$CN; 85%-H$_3$PO$_4$) 73.70 (s, J_{PSe} 579.1, J_{PC} 36.1); δ_{Se} (38.1 MHz; CD$_3$CN; Me$_2$Se) −466.70 (d, J_{SeP} 579.8).

‡ *Crystal data*: **2**: $C_{22}H_{54}Ag_2N_2O_8P_2S_4Te_2$; $M_r = 1135.8$, monoclinic, space group $P2_1/n$, $a = 11.7663(15)$, $b = 7.794(2)$, $c = 21.802(4)$ Å, $\beta = 105.457(15)°$, $V = 1927.1(6)$ Å^3, $Z = 2$, $T = 143$ K, $\mu = 2.841$ mm^{-1}; pale yellow block. Of 3602 reflections measured, 3396 were independent ($R_{int} = 0.0208$). Final $R1 = 0.0359$, w$R2 = 0.0594$ (all data).

3 (acetonitrile solvate): $C_{42}H_{99}Ag_2N_3O_8P_4S_4Te_4$; $M_r = 1752.50$, monoclinic, space group $P2_1/n$, $a = 11.4760(15)$, $b = 15.363(3)$, $c = 38.378(3)$ Å, $\beta = 93.962(10)°$, $V = 6749.9(15)$ Å^3, $Z = 4$, $T = 143$ K, $\mu = 2.536$ mm^{-1}; pale yellow block. Of 12 445 reflections measured, 11 815 were independent ($R_{int} = 0.0387$). Final $R1 = 0.0838$, w$R2 = 0.1086$ (all data).

5: $C_{18}H_{42}AgF_6P_2SbTe_2$; $M_r = 919.28$, monoclinic, space group $P2_1/c$, $a = 28.5566(15)$, $b = 8.4221(5)$, $c = 28.2425(15)$ Å, $\beta = 118.884(1)°$, $V = 5947.5(6)$ Å^3, $Z = 8$ (monomers), $T = 143$ K, $\mu = 3.640$ mm^{-1}; yellow prism. Of 107 897 reflections measured, 15 108 were independent ($R_{int} = 0.0850$). Final $R1 = 0.0910$, w$R2 = 0.0957$ (all data).

6: $C_{18}H_{42}AgF_6P_2SbSe_2$; $M_r = 822.00$, monoclinic, space group $P2_1/n$, $a = 8.6889(6)$, $b = 23.6812(16)$, $c = 13.6253(10)$ Å, $\beta = 92.965(3)°$, $V = 2799.8(3)$ Å^3, $Z = 4$, $T = 143$ K, $\mu = 4.423$ mm^{-1}; colourless prism. Of 59 721 reflections measured, 8562 were independent ($R_{int} = 0.0748$). Final $R1 = 0.0341$, w$R2 = 0.0709$ (all data).

Data were recorded using Mo Kα radiation ($\lambda = 0.71073$ Å) on a Stoe STADI-4 (**2**, **3**; $2\theta_{max}$ 50°) or Bruker SMART 1000 CCD diffractometer (**5**, **6**; $2\theta_{max}$ 56°, 61°). Refinements were performed with the program SHELXL-97.[13] CCDC 611403 (**2**), 611440 (**3**), 636033 (**5**), 636034 (**6**). For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b700917h

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