

Billups, M. A. Ciufolini), VCH, Weinheim, 1993; c) *Von Fuller bis zu Fullerenen, Beispiele einer interdisziplinären Forschung* (Eds.: W. Krätschmer, H. Schuster), Vieweg, Braunschweig, 1996.

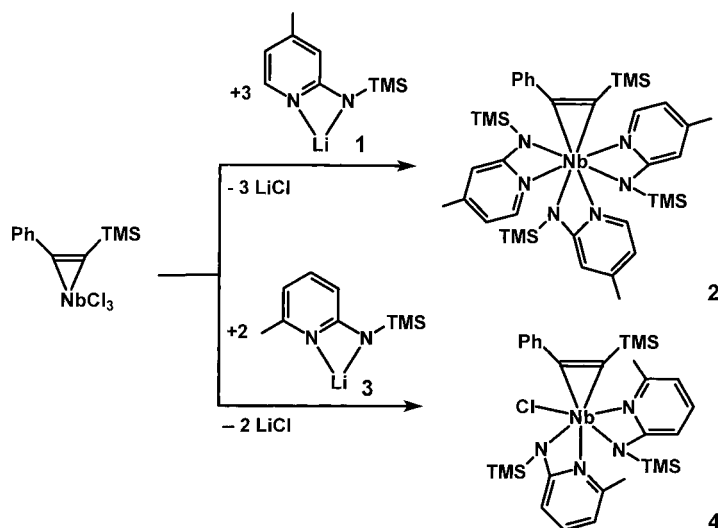
- [8] M. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247–422.
- [9] Spherical viruses display a 60-fold identically packed fundamental structural motif that can formally be assigned to pentagonal and also hexagonal capsomers (morphology units or chemically definable oligomers of one or more viral proteins or subunits). The most simple example is presented by the satellite tobacco necrosis virus (Figure 5), in which only 12 pentagonal capsomers with a total of 60 identical viral proteins (subunits) coded by one gene only are placed at the 12 corners of an icosahedron. In the case of the larger spherical viruses—for example, those with  $3 \times 60 = 180$  subunits—the motif that occurs 60 times shows (different) subunits organized in capsomers of five identically connected protein monomers (pentagons) centered at the corners and 20 additional capsomers (hexagons) built up by six protein monomers (see Figure 1). In accordance with Caspar and Klug<sup>[10a, b]</sup> the triangular faces of an icosahedron can be subdivided into an integral number of equilateral triangles. This procedure demonstrates that the “normal” spherical viruses, such as that of the TBSV (tomato bushy stunt virus) can have more than 60 subunits (which is also the case for **1a**). The resulting solid is an icosadeltahedron (a capped icosahedron is such a solid) with local symmetry elements that relate to its subunits in addition to the exact symmetry elements of the icosahedron. (Subunits that are distributed about each exact triangular vertex of a  $T=3$  icosadeltahedron are related by a local  $C_6$  symmetry axis; corresponding adjacent subunits are only quasi-equivalent.) The number of subunits in an icosadeltahedron equals  $60T$  (where  $T = h^2 + hk + k^2$  denotes the triangulation number, which is important for the architecture of viruses;  $h$  and  $k$  are integers<sup>[10a, d, h]</sup>). A virus structure with  $T=3$  (Figure 1) resembles  $180 (= 3 \times 60)$  subunits (for  $h=k=1$ ) whereas the triangulation number  $T=1$  (with  $h=1, k=0$ ) stands for the only 10 nm large satellite tobacco necrosis virus, and also for the fragment of **1a** with its 60  $\{\text{MoO}_6\}$  octahedral subunits of the 12  $\{\text{(Mo)Mo}_5\}$  pentagons. For a known, topologically comparable geodesic dome of Fuller  $T=36$ <sup>[10a]</sup> (for extensive literature on this subject see reference [10]).
- [10] a) See D. Voet, J. G. Voet, *Biochemie*, VCH, Weinheim, 1992; see also A. Müller, C. Beugholt, *Nature* **1996**, *383*, 296–297; b) B. Alberts, D. Bray, J. Lewis, M. Raff, K. Roberts, J. D. Watson, *Molekularbiologie der Zelle*, VCH, Weinheim, 1990; c) B. D. Davis, R. Dulbecco, H. N. Eisen, H. S. Ginsberg, *Microbiology*, Harper, Philadelphia, 1980, p. 869; d) “The Structure of Satellite Tobacco Necrosis Virus”: L. Liljas, B. Strandberg in *Biological Macromolecules and Assemblies, Vol. 1, Virus Structures* (Eds.: F. A. Jurnak, A. McPherson), Wiley, New York, 1984, pp. 97–119; e) L. Liljas, T. Unge, T. A. Jones, K. Fridborg, S. Lövgren, U. Skoglund, B. Strandberg, *J. Mol. Biol.* **1982**, *159*, 93–108; f) S. C. Harrison, *Trends Biochem. Sci.* **1984**, 345–351; g) H. G. Schlegel, *Allgemeine Mikrobiologie*, Thieme, Stuttgart, 1992; h) D. L. D. Caspar, A. Klug, *Cold Spring Harbor Symp. Quant. Biol.* **1962**, *27*, 1–24; i) M. Kemp, *Nature*, 1998, 396, 123.
- [11] This leads to the presence of the fivefold degenerate irreducible representation  $H_g$  (F. A. Cotton, *Chemical Applications of Group Theory*, 3rd ed., Wiley, New York, 1990), for example with the consequence of only a few bands in the IR and Raman spectra.
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- [15] There is also an additional, but marginal relationship to Kepler's conjectures of 1611 that no packing of spheres can be denser than in the face-centered-cubic lattice, observed for instance in crystals of **1**, a conjecture that could only now be confirmed (see N. J. A. Sloane, *Nature* **1998**, 395, 435–436).

## Novel Amidoniobium Complexes with a Functional Relationship to the $[\text{Cp}_2\text{ZrR}]^+$ Ion\*

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Niobium and tantalum compounds live in the shadow of metal complexes of Group 4. Possible reasons for this are the extremely interesting applications of the latter compounds in olefin polymerization<sup>[1]</sup> or in selective couplings of  $\alpha$ -olefins for organic synthesis.<sup>[2]</sup> Hopes of catalysts with more versatility with regard to the functional groups of the olefins which are to be coupled have recently stimulated increased activity in the search for catalytically active species in Group 5;<sup>[3]</sup> for analogues of the known  $[\text{Cp}_2\text{MR}]^+$  ions ( $M = \text{Ti}, \text{Zr}, \text{Hf}$ ). Amido ligands might be useful in this respect.<sup>[4]</sup> Herein we report the first cationic amidoniobium compound, which can be used for selective coupling of  $\alpha$ -olefins.

Treatment of  $[\text{NbCl}_3(\text{dme})(\text{PhC}\equiv\text{TMS})]$ <sup>[5]</sup> ( $\text{dme}$  = dimethoxyethane,  $\text{TMS}$  = trimethylsilyl) with **1** (3 equiv) gave the orange-red alkyne-niobium complex **2** (Scheme 1). The IR spectrum and the  $^{13}\text{C}$  NMR data of **2** indicate that the alkyne



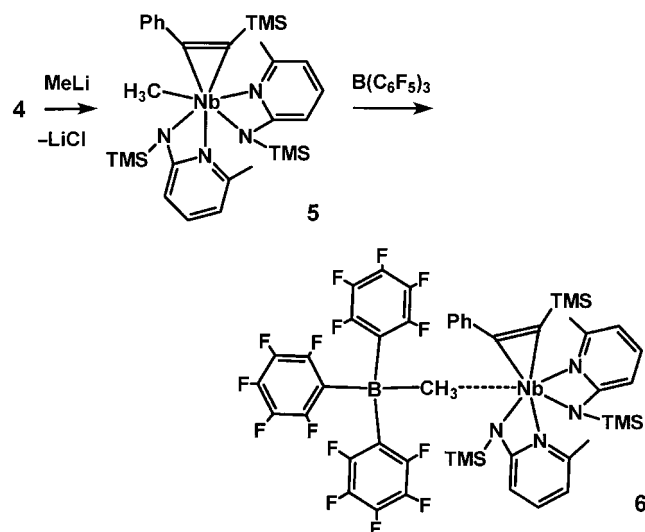
Scheme 1. Synthesis of **2** and **4**.

ligand functions as a 4e donor.<sup>[6]</sup> The niobacyclopropene ring in **2** is extremely stable and does not react with ketones, styrene oxide, alkynes, and olefins, as known for the metal-locene alkyne complexes of the titanium triad.<sup>[7]</sup> Complexes with only two amido ligands are accessible by using the sterically more demanding aminopyridinato (Ap) ligands.

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Thus, the otherwise analogous reaction of  $[\text{NbCl}_3(\text{dme})-(\text{PhC}\equiv\text{CTMS})]$  with **3** (2 equiv) led to **4**. Treatment of **4** with MeLi gave the alkyl complex **5** (Scheme 2). In this reaction



Scheme 2. Synthesis of **5** and **6**.

there are no indications of an attack at the coordinated alkyne or at the Ap ligands. The NMR spectra of **4** and **5** contain four sets of signals for the Ap ligands and two for the coordinated alkyne units. When the temperature is raised, two sets of Ap and one set of alkyne signals result in coalescence. Hence, two isomers exist in solution, which interconvert by ligand rotation on the NMR timescale. In addition, the two Ap ligands of the two isomers occur in chemically different environments and do not exchange within the temperature range examined. The X-ray structure analysis<sup>[8]</sup> of **5** reveals that two independent molecules are present in the asymmetric unit in the solid state; the alkyne ligands adopt different orientations with respect to the Ap–Nb fragment (Figure 1). Thus it is assumed that the two isomers observed in solution interconvert by alkyne rotation. Taking into consideration this assumption the activation barrier for rotation of the alkyne for **4** is  $\Delta G^\ddagger = 80 \text{ kJ mol}^{-1}$ .

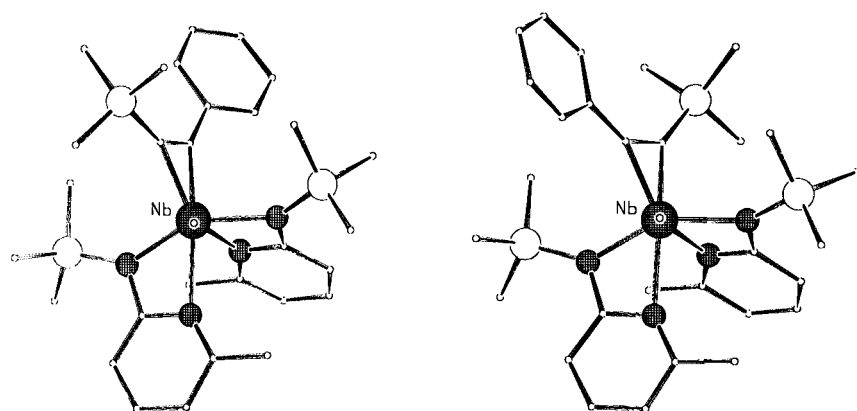


Figure 1. Molecular structures of both isomers of **5** in the crystal. View along the C(methyl)–Nb bond (the H atoms are omitted). Selected bond lengths [Å] (average values): Nb–C<sub>Me</sub> 2.195(13), C–C(alkyne) 1.32(2).

The reaction of **5** with  $\text{B}(\text{C}_6\text{F}_5)_3$  led to **6** (Scheme 2), whose NMR spectrum ( $\text{C}_6\text{D}_5\text{Br}$ ) confirmed that an alkyne rotation also took place in this case. Compound **6** is the first X-ray structurally characterized<sup>[8]</sup> “zwitterionic” compound of a metal in Group 5, in which an apical alkyl ligand was partially abstracted by a borane (Figure 2). Similar compounds have

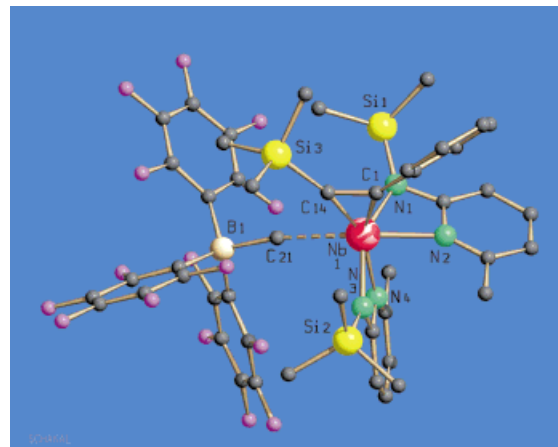


Figure 2. Molecular structure of **6** in the crystal. Selected bond lengths [Å] and angles [°]: C1–C14 1.313(6), C1–Nb1 2.081(4), C14–Nb1 2.117(4), C21–B1 1.671(6), C21–Nb1 2.611(5), N1–Nb1 2.105(4), N2–Nb1 2.218(3), N3–Nb1 2.058(3), N4–Nb1 2.353(4), C1–Nb1–C14 36.4(2), N1–Nb1–N2 62.24(14), N3–Nb1–N4 60.96(13), N3–Nb1–C21 96.23(14), N1–Nb1–C21 95.23(14), N4–Nb1–C21 78.16(13).

been described for metal complexes of the titanium triad<sup>[9]</sup> and are considered for comparison. The Nb–C(Me<sub>bridge</sub>) distance of 2.611(5) Å resembles otherwise analogous Zr–C distances in zirconocenes (2.55–2.67 Å).<sup>[9]</sup> The same is true for the B–C(Me<sub>bridge</sub>) distance. The C–C distance of the coordinated alkyne in **6** is 1.313(6) Å. This value is very similar to that of a  $\text{C}(\text{sp}^2)=\text{C}(\text{sp}^2)$  bond (1.321(13) Å)<sup>[10]</sup> and is expected for an alkyne functioning as a 4e donor. The compound **6** polymerizes ethene to polyethylene (PE) as a one-component system without addition of cocatalyst. However, the catalyst decomposes very rapidly under the reaction conditions ( $t = 4 \text{ h}$ ,  $n_{\text{cat}} = 0.5 \text{ mmol L}^{-1}$ ,  $T = 80^\circ\text{C}$ ,  $p_{\text{ethene}} = 6.5 \text{ bar}$ ). This can be prevented by the addition of a little  $i\text{Bu}_3\text{Al}$  as scavenger (activity:  $4.4 \text{ kg}_{\text{PE}} \text{ mol}_{\text{Nb}}^{-1} \text{ h}^{-1}$ ).<sup>[11]</sup> The narrow mol mass distribution ( $M_w/M_n = 1.8$ ) supports the presence of a uniform catalyst species. The average mol mass of  $36000 \text{ g mol}^{-1}$  of the polymers obtained in the ethylene polymerization is low and illustrates the tendency for rapid chain breakage. 1-Butene can be selectively (98%) dimerized ( $\text{TOF} = 1200 \text{ h}^{-1}$ ) to give 2-ethylhexene with **6** at room temperature in the presence of methylalumoxane (MAO, 120 equiv). The reactivity of cationic aminopyridinato-niobium and -tantalum alkyne complexes such as **6** is currently under investigation.

# Experimental Section

All experiments were carried out under argon with exclusion of oxygen and moisture.

**2:** 4-Methyl-2-trimethylsilylamino-pyridine (638  $\mu$ L, 3 mmol) in hexane (20 mL) was treated with 2.5 M *n*BuLi in hexane (1.2 mL, 3 mmol) at  $-78^{\circ}\text{C}$ , and stirred for 2 h at room temperature. The resulting solution was added to a suspension of  $[\text{NbCl}_3(\text{dme})(\text{PhC}\equiv\text{CTMS})]$  (464 mg, 1 mmol) in hexane (20 mL). This mixture was stirred for 16 h at room temperature, precipitated LiCl was filtered off, and the filtrate was concentrated under vacuum. Orange, crystalline **2** (435 mg, 54 %) was obtained at  $-30^{\circ}\text{C}$ ; m.p.:  $212^{\circ}\text{C}$ ; elemental analysis ( $\text{C}_{38}\text{H}_{59}\text{NbSi}_4$ , 805.18): calcd.: C 56.69, H 7.39, N 10.44; found: C 56.76, H 7.67, N 10.57;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 297 K):  $\delta$  = 8.36, 7.69, 6.94 (3 d,  $J$  = 5.6 Hz, each 1 H, H-6, Ap), 7.76, (d, 2 H, *o*-H, Ph), 7.24 (tr, 2 H, *m*-H, Ph), 7.04 (tr, 1 H, *p*-H, Ph), 6.22 (br., 2 H, H-3, Ap), 6.07, 5.98, 5.82 (3 d, each 1 H, H-5, Ap), 6.03 (s, 1 H, H-3, Ap), 1.96, 1.81, 1.75 (br., each 3 H, Me-Ap), 0.46, 0.28, 0.11,  $-0.15$  ( $4 \times$  s, each 9 H, SiMe<sub>3</sub>);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 297 K):  $\delta$  = 223.1 (CSiMe<sub>3</sub>), 209.1 (CPh), 170.3, 169.8, 167.9 (C-2, Ap), 149.8, 147.7, 147.5 (C-4, Ap), 148.1, 145.5, 143.6 (C-6, Ap), 140.0 (*ipso*-C, Ph), 132.0, 128.4, 128.3 (*o*-, *m*-, *p*-C, Ph), 114.7, 113.6, 112.1, 111.6, 108.3, 107.4 (C-3, C-5, Ap), 21.6, 21.5, 21.4 (Me, Ap), 2.2, 1.6, 1.3, 1.3 (SiMe<sub>3</sub>); IR (Nujol):  $\tilde{\nu}$  = 1645  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ , coordinated).

**4:** 6-Methyl-2-trimethylsilylamino-pyridine (850  $\mu$ L, 4 mmol) in hexane (20 mL) was treated with 2.5 M *n*BuLi in hexane (1.6 mL, 4 mmol) at  $-78^{\circ}\text{C}$ , and stirred for 2 h at room temperature. The resulting solution was added to a suspension of  $[\text{NbCl}_3(\text{dme})(\text{PhC}\equiv\text{CTMS})]$  (927 mg, 2 mmol) in hexane (20 mL). This mixture was stirred for 16 h at room temperature, precipitated LiCl was filtered off, and the filtrate was concentrated under vacuum. Compound **4** crystallized in the form of red prisms at  $-30^{\circ}\text{C}$  (1.044 g, 79 %); m.p.:  $137^{\circ}\text{C}$ ; elemental analysis ( $\text{C}_{29}\text{H}_{44}\text{NbSi}_3\text{Cl}$ , 661.31): calcd.: C 52.67, H 6.71, N 8.47; found: C 52.71, H 6.55, N 8.63;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 297 K):  $\delta$  = 8.52 (dd, 2 H, Ap), 7.45 (dd, 2 H, Ap), 7.36 (tr, 2 H, Ap), 7.15–7.10 (m, 2 H, Ap + Ph), 6.9–6.7 (m, 2 H, Ap + Ph), 6.08–5.86 (m, 5 H, Ap + Ph), 2.33, 2.29, 2.09, 1.92 (4 s, each 3 H, Me-Ap), 0.76, 0.24, 0.29, 0.23, 0.13, 0.02 (6 s, each 9 H, SiMe<sub>3</sub>);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 297 K):  $\delta$  = 227.1 (CSiMe<sub>3</sub>), 163.9, 164.1, 162.7, 162.4 (C-2, Ap), 156.0, 155.6, 155.1, 154.9 (C-6, Ap), 142.0, 138.9 (*ipso*-C, Ph), 139.7, 139.6, 138.0, 137.9 (C-4, Ap), 133.2, 129.4, 128.9, 128.7, 128.5, 128.3 (*o*-, *m*-, *p*-C, Ph), 115.9, 115.7, 111.5, 111.2, 107.9, 107.6, 105.6, 105.4 (C-3, C-5, Ap), 23.5, 23.4, 21.4, 21.4 (Me, Ap), 2.1, 2.0, 1.9, 1.8, 0.08 (SiMe<sub>3</sub>); the second quaternary C atom of the alkyne was not detected. Two isomers are present at room temperature in the ratio 1:1; IR (Nujol):  $\tilde{\nu}$  = 1643  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ , coordinated).

**5:** A solution of **4** (661 mg, 1 mmol) in hexane (10 mL) was treated with 1.6 M MeLi (625  $\mu$ L, 1 mmol) at  $-40^{\circ}\text{C}$ , and stirred for 2 h at room temperature. The reaction solution was filtered and the filtrate was concentrated under vacuum. Red crystalline **5** (327 mg, 51 %) was obtained at  $-30^{\circ}\text{C}$ ; m.p.:  $168^{\circ}\text{C}$ ; elemental analysis ( $\text{C}_{30}\text{H}_{47}\text{NbSi}_4$ , 640.89): calcd.: C 56.22, H 7.39, N 8.74; found: C 56.24, H 7.44, N 9.18;  $^1\text{H}$  NMR ( $[\text{D}_8]\text{toluene}$ , 230 K):  $\delta$  = 8.01, 7.52 (d, H-3, Ap), 7.32, 7.08, 6.87, 6.73, 5.95–5.86 (m, Ph + Ap), 5.81 (dd, H-5, Ap), 2.24, 2.22, 2.01, 1.88, 1.61, 1.58 (br., each 3 H, Me), 0.65, 0.27, 0.12, 0.08, 0.07,  $-0.03$  (br., each 9 H, SiMe<sub>3</sub>);  $^{13}\text{C}$  NMR ( $[\text{D}_8]\text{toluene}$ , 230 K):  $\delta$  = 235.3, 235.1 (CSiMe<sub>3</sub>), 165.0, 165.0, 164.9, 164 (C-2, Ap), 155.5, 155.2, 155.1, 155.0 (C-6, Ap), 142.0, 138.8 (*ipso*-C, Ph), 139.9, 139.8, 139.6, 137.9, 137.8, 137.6, 137.5 (C-4, Ap, *o*-, *m*-, *p*-C, Ph), 114.7, 114.5, 110.1, 109.9, 107.7, 107.5, 105.8, 105.6 (C-3, C-5, Ap), 23.5, 23.4, 23.3 (Me), 2.1, 1.9, 1.4, 1.8, 1.7, 1.6 (SiMe<sub>3</sub>); two isomers are present in solution at 230 K in the ratio 2:1; IR (Nujol):  $\tilde{\nu}$  = 1622  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ , coordinated).

**6:** A solution of **5** (641 mg, 1 mmol) in toluene (10 mL) was treated with  $\text{B}(\text{C}_6\text{F}_5)_3$  (512 mg, 1 mmol) in toluene (10 mL). The mixture was stirred briefly, filtered, and the volume of the filtrate was concentrated to about half. Compound **6** was obtained as a red powder (1.083 mg, 94 %) at  $-30^{\circ}\text{C}$ . M.p.:  $172^{\circ}\text{C}$ ; elemental analysis ( $\text{C}_{48}\text{H}_{47}\text{NbSi}_3\text{BF}_{15}$ , 1152.88): calcd.: C 50.01, H 4.11, N 4.86; found: C 49.90, H 4.32, N 4.86;  $^1\text{H}$  NMR ( $[\text{D}_5]\text{bromobenzene}$ , 320 K):  $\delta$  = 7.2–7.1, 6.8 (m, 7 H, Ph, Ap), 5.95 (d, 2 H, Ap), 5.88 (d, 2 H, Ap), 1.44 (s, 6 H, Me), 0.96 (s, 3 H, Me), 0.14 (s, 9 H, SiMe<sub>3</sub>),  $-0.07$  (s, 18 H, SiMe<sub>3</sub>);  $^{19}\text{F}$  NMR ( $[\text{D}_5]\text{bromobenzene}$ , 297 K):  $\delta$  = 182.9 (tr, *m*-F), 179.6 (tr, *p*-F), 147.1 (d, *o*-F); IR (Nujol):  $\tilde{\nu}$  = 1641  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ , coordinated).

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- [8] Structure analyses of **5** and **6**: STOE-IPDS diffractometer, graphite-monochromated  $\text{MoK}\alpha$  radiation,  $\lambda$  = 0.71069 Å, structure solution with direct methods (SHELXS-86: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467), refinement with full-matrix least-squares methods against  $F^2$  (SHELXL-93: G. M. Sheldrick, unpublished results), structure representation: XP (Siemens). **5**: Crystal dimensions  $0.4 \times 0.3 \times 0.2$  mm<sup>3</sup>, orange prisms, space group  $P2_1$ , monoclinic,  $a$  = 18.500(2),  $b$  = 11.376(1),  $c$  = 18.905(2) Å,  $\beta$  = 118.38(1) $^\circ$ ,  $V$  = 3500.5(7) Å<sup>3</sup>,  $Z$  = 2,  $\rho_{\text{calcd}}$  = 1.216 g cm<sup>−3</sup>, 10535 measured, 10360 independent reflections, 6543 of which were considered as observed ( $I \geq 2\sigma(I)$ ),  $R$  = 0.046,  $wR^2$  = 0.110 (all data), 685 parameters. **6**: Crystal dimensions  $0.5 \times 0.4 \times 0.2$  mm<sup>3</sup>, red prisms, space group  $P\bar{1}$ , triclinic,  $a$  = 12.420(2),  $b$  = 16.994(2),  $c$  = 17.934(3) Å,  $\alpha$  = 77.12(1),  $\beta$  = 74.72(1),  $\gamma$  = 71.75(1) $^\circ$ ,  $V$  = 3426.8(9) Å<sup>3</sup>,  $Z$  = 2,  $\rho_{\text{calcd}}$  = 1.385 g cm<sup>−3</sup>, 10273 measured, 10273 symmetry-independent reflections, 8046 of which were considered as observed ( $I \geq 2\sigma(I)$ ),  $R$  = 0.054,  $wR^2$  = 0.174 (all data), 785 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101948 (**5**) and CCDC-101949 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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- [11] Compound **6**, for example, is stable in  $\text{C}_6\text{D}_6$  for 8 h at  $80^{\circ}\text{C}$  without significant decomposition (NMR experiment).