

Syntheses and reactivity of novel unsaturated cyclic compounds containing phosphorus atoms

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Abstract

Kinetic stabilization of compounds containing heavy main-group elements through the use of bulky substituents is of current interest. The widely used 2,4,6-tri-*t*-butylphenyl group (Mes*) is recognized as a powerful bulky protecting group and has enabled us to successfully prepare various types of phosphorus compounds with unusual structures. When a phosphalkyne carrying Mes* was treated with *t*BuLi and then quenched with MeOH, a 1,3-diphosphacyclobutene was obtained, whereas, when MeI was used as a quencher, a 1,3-diphosphacyclobutane-2,4-diyl was formed almost quantitatively as a stable biradical compound. The reaction mechanism for the formation of both compounds can be explained by a phosphide intermediate, which can be formed via dimerization of the phosphalkyne promoted by *t*BuLi. Some other diphosphacyclobutane-2,4-diyls with various substituents were prepared in a similar fashion and showed interesting reactivities including ring expansion, oxidation, isomerization and so on.

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1. Introduction

Phosphorus compounds containing unusual bonding have been accomplished by the introduction of bulky substituents as protecting groups [1]. Phosphalkynes with P≡C bonding protected by 2,4,6-tri-*t*-butylphenyl groups (**1**) [2] as well as *t*-butyl groups (**2**) [3] have been prepared and various reactions have been reported to date [4]. The chemistry of low-coordinated phosphorus is no longer unusual and it is even considered that phosphorus is the carbon copy [5]. Here we describe the unusual character of several unsaturated phosphorus containing cyclic compounds (see Chart 1).

2. Results and discussion

2.1. Reaction of arylphosphalkyne with alkyllithium compound

2.1.1. Formation of 1,3-diphosphacyclobutene

Phosphalkyne **1** was allowed to react with 0.5 equiv. of *t*-butyllithium followed by quenching with methanol in THF at −78 °C to afford 1,3-diphosphacyclobutene **3** in 41% yield (Scheme 1) [6]. The structure of **3** was unambiguously determined by X-ray analysis, the result of which was different from that reported by Cowley and co-workers [7].

2.1.2. Formation of 1,3-diphosphacyclobutane-2,4-diyl

The formation of 1,3-diphosphacyclobutene **3** indicates that dimerization of phosphalkyne **1**, assisted by addition of *t*-butyllithium followed by cyclization, occurs to give intermediate **4**. Interestingly, when methyl

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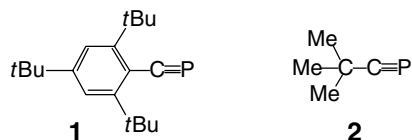
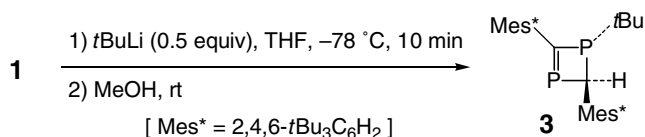


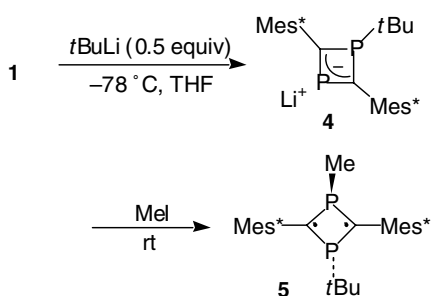
Chart 1.



Scheme 1.

iodide was used as a quencher in place of methanol, 1,3-diphosphacyclobutane-2,4-diyl (**5**) was obtained as a stable compound of deep blue color almost quantitatively (Scheme 2) [8]. The structure of **5** was confirmed by X-ray analysis. It is remarkable that the diyl **5** is stable at room temperature in air. The cyclic voltammogram of **5** showed a reversible oxidation peak at +0.35 V (versus Ag/AgCl) probably due to the oxidation at the carbon radical centers, which might correspond to the HOMO [8].

The framework of **5** is very much similar to that of biradical species **6A** reported by Niecke et al. [9a]. Very recently, boron-based biradical species **7** has been reported by Bertrand and co-workers [10]. The biradical species is believed to take a singlet biradical based on the theoretical studies by Schoeller et al. [11]. The chemistry of such species involving heteroatoms is of current interest [12]. As discussed in Section 2.2, our method for the preparation of diphosphadiyls is general and straightforward (see Chart 2).



Scheme 2.

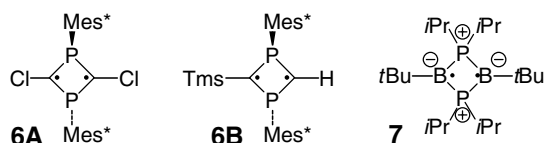
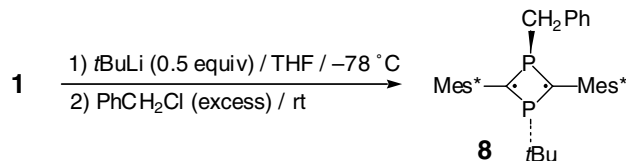


Chart 2.



Scheme 3.

2.1.3. X-ray structure of *P*-benzyl-1,3-diphosphacyclobutane-2,4-diyl

Very similarly, the diyl species **8** with a benzyl moiety was prepared by quenching **4** with benzyl chloride as a very stable deep-blue violet compound (Scheme 3).

The structure was determined by X-ray analysis with higher resolution than that for **5**. Fig. 1 shows the molecular structure of **8** [13]. The crystal data and some selected bond lengths and angles are listed in Tables 1 and 2 together with those for **5**. The four-membered ring geometry of **8** was almost the same as that of **5**. The two carbon atoms take a flat configuration of sp^2 hybridization and the phosphorus atoms are pyramidalized. The bond distance between the two phosphorus atoms is 2.44 Å, and that between the two carbon atoms is 2.53

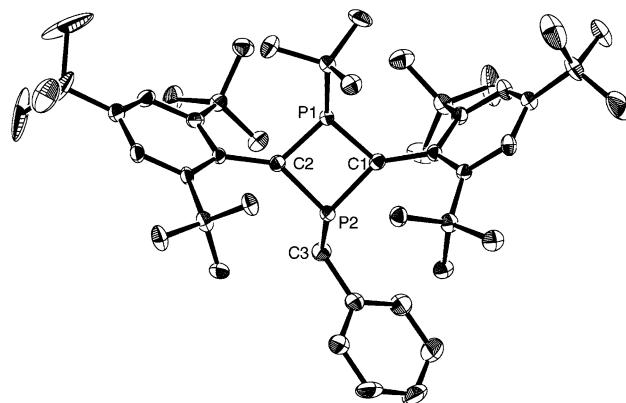


Fig. 1. Molecular structure of **8** with 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 1
Crystal data for **8** · 3CHCl₃ and **5**^a

	8 · 3CHCl ₃	5
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$ (#19)	$P\bar{1}$ (#2)
<i>a</i> (Å)	17.5373(4)	14.553(2)
<i>b</i> (Å)	28.7617(6)	14.480(3)
<i>c</i> (Å)	1.3338(2)	8.878(3)
α (°)	90	96.64(1)
β (°)	90	104.94(2)
γ (°)	90	106.81(2)
<i>V</i> (Å ³)	5716.8(2)	2044.2(8)
<i>Z</i>	4	2
<i>R</i>	0.064	0.099
<i>R</i>	0.084	0.136
CCDC No.	242210	208433

^a Data for **5** were taken from [8].

Table 2

Selected bond lengths (Å) and angles (°) for **8** and **5**^a

	8 ·3CHCl ₃	5
P1–C1	1.718(5)	1.70(1)
P1–C2	1.713(5)	1.72(1)
P1– <i>t</i> Bu	1.866(6)	1.877(10)
P2–C1	1.811(5)	1.77(1)
P2–C2	1.797(5)	1.79(1)
P2–Me	1.893(6) ^b	1.85(1)
C1–Mes*	1.481(7)	1.50(1)
C2–Mes*	1.488(7)	1.49(1)
C1–P1–C2	95.1(2)	94.0(5)
C1–P1– <i>t</i> Bu	125.2(3)	123.1(5)
C2–P1– <i>t</i> Bu	123.9(3)	124.3(5)
C1–P2–C2	89.1(2)	89.1(5)
C1–P2–C3	116.5(2)	116.0(5)
C2–P2–C3	112.3(3)	113.9(5)
P1–C1–P2	87.5(2)	89.0(5)
P1–C1–Mes*	126.9(4)	127.5(7)
P2–C1–Mes*	142.8(4)	143.3(7)
P1–C2–P2	88.1(2)	87.6(5)
P1–C2–Mes*	129.7(4)	126.2(7)
P2–C2–Mes*	142.4(4)	144.4(7)
∑P1	344.2	341.4
∑P2	317.9	319.0
∑C1	357.2	359.8
∑C2	360.2	358.2
C1...C2	2.53	2.50
P1...P2	2.44	2.43

^a Data for **5** were taken from [8].^b Bond length of P2–C3 for **8**.

Å, indicating no apparent angular interactions among them in the crystalline state. Although we observed the P–C bond-length differences around P1 and P2, in contrast to the equal bond lengths for **6A**, but similar to another example by Niecke **6B** [9b], these differences do not directly suggest a large contribution of **18B** as de-

scribed in Section 2.2, since the P atoms in **8** do not take the flat configuration, which is required for **18B**.

2.2. Reactions of 1,3-diphosphacyclobutane-2,4-diyls

Niecke et al. [14] have reported various interesting reactions of diyls involving carbene intermediates. Thermal reaction of either **5** or **8** in toluene at 100 °C for 3 h gave phosphalkyne **1** in a fair to good yield. In the thermolysis of **5**, isobutene was formed as byproduct as observed by ¹H NMR study.

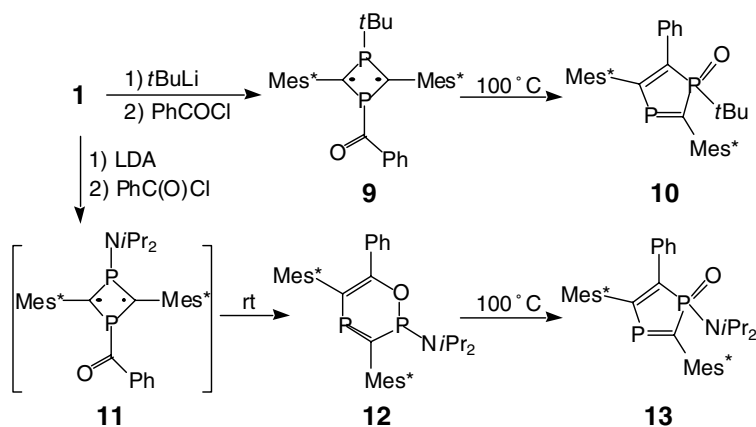
We have observed that thermal reactions of amino- and carbonyl-substituted diyls **9** and **11** occurred at 100 °C to give ring expansion products **10** and **13**, respectively (Scheme 4). The five-membered products seemed to be formed via the Arbuzov-type reaction of cyclic six-membered amidophosphonite such as **12**. The structures of **10**, **12** and **13** are new ring systems and were determined by X-ray analysis [15].

Diyl **14** gave hydrolysis products **15** and **16** in almost equal amount, the structures of which were determined unambiguously by X-ray analysis (Scheme 5) [15].

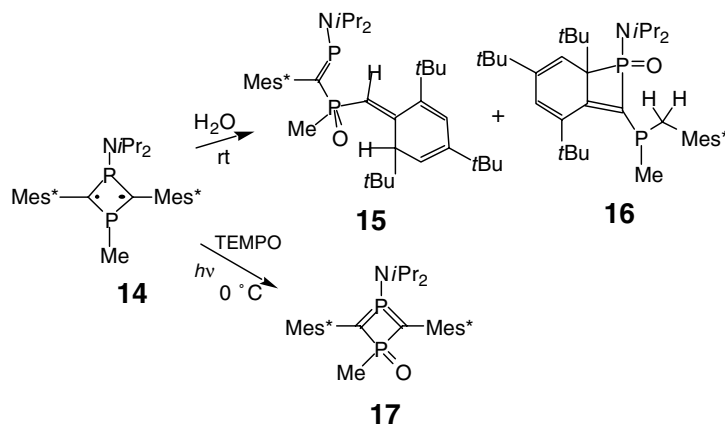
Interestingly, **14** gave **17** in the presence of tetramethylpiperidinoxyl (TEMPO) on exposure to light [15]. The structure was confirmed by X-ray analysis and it takes **18B**, one of the interesting canonical formulae proposed by theoretical studies of **18** [11]. The X-ray structure shows that the phosphorane P is almost perfectly flat with ∑(angles) = 359.9°. This is the first example of a four-membered dimethylenephosphorane in contrast to an acyclic compound, Me₂NP(=CTms)₂ [16] (see Chart 3).

2.3. Formation of 1,4-diphosphafulvene

It is interesting to note that the reaction of 1-phosphaallene precursor **20** with *t*-butyllithium (Scheme 6) gave 1,4-diphosphafulvene (31%) together with 1-phosphaallene **22** (2%) and 3,4-diphosphinidenecyclobutene



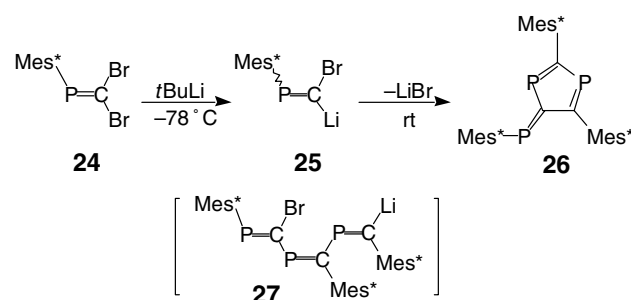
Scheme 4.



(DPCB) **23** (6%) [17]. The formation of **21** is explainable by the formal dimerization of **22** in [2 + 3]-fashion. DPCB **23** appears to be formed by another route of dimerization of **20**. The fulvene **21** is also a new heterocyclic compound with an interesting π -system [18].

2.4. Formation of 1,3,6-triphosphafulvene

2,2-Dibromophosphaethene **24** was allowed to react with *t*-butyllithium at $-78\text{ }^\circ\text{C}$ to give a new 6- π cyclic compound **26** in 59% yield (Scheme 7) [19]. The reaction appears to involve the addition of **25** to two equivalents of phosphalkyne **1** generated under the reaction conditions [20] forming an intermediate **27**.



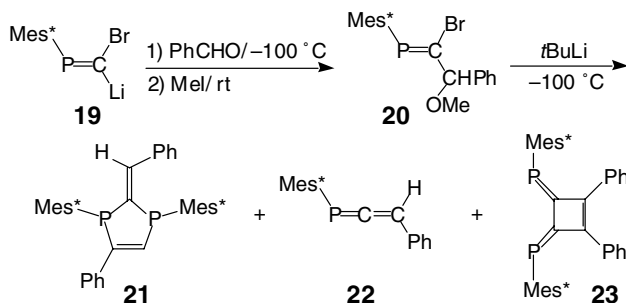
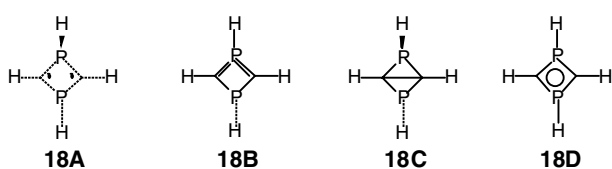
3. Conclusion

We have described the syntheses and reactivity of novel unsaturated cyclic compounds containing phosphorus suggesting the usefulness of 2,4,6-tri-*t*-butylphenyl (Mes*) as a protecting group. Among those, the structure of 1,3-diphospha-cyclobutane-2,4-diyl with a singlet biradical at the carbon atoms in the four-membered ring was confirmed by X-ray crystallography and reactions were conducted to explore the character of the unusual bonding system.

4. Experimental

4.1. General

All manipulations were carried out under an argon atmosphere by means of standard Schlenk techniques. All solvents employed were dried by appropriate methods. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AVANCE400 spectrometer in CDCl_3 with Me_4Si (^1H , ^{13}C) and H_3PO_4 (^{31}P), respectively, as an internal or external standard. Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. Elemental analyses were performed in the Instrumental Analysis Center for



Chemistry, Graduate School of Science, Tohoku University.

4.2. Preparation of **8**

Phosphaalkyne **1** was prepared by procedures described in the literature [8]. To a solution of **1** (300 mg, 1.0 mmol) in THF (8 mL) was added *t*-butyllithium (0.57 mmol, 0.38 mL of a 1.5 M solution in pentane) at $-78\text{ }^{\circ}\text{C}$ and the mixture was stirred for 15 min. The mixture was then allowed to warm to room temperature and allowed to react with benzyl chloride (0.1 mL, 0.90 mmol) for 2 h. The solvent was removed in vacuo. The residual material was extracted with dichloromethane and washed with hexane to afford 370 mg of **8** almost quantitatively. Compound **8** was stable at room temperature in air and no decomposition was observed after 1 week. Solubility in the common organic solvents is poor compared to that of **5**.

Bright violet plates (CHCl_3): m.p. 155–156 $^{\circ}\text{C}$ (decomp.). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) $\delta = 58.1$ (d, $^2J_{\text{PP}} = 334.8$ Hz, *PtBu*), 0.55 (d, $^2J_{\text{PP}} = 334.8$ Hz, PCH_2Ph); ^1H NMR (400 MHz, CDCl_3) $\delta = 7.44$ (s, 2H, *m*-Mes*), 7.24 (s, 2H, *m*-Mes*), 7.08–7.19 (m, 5H, Ph), 3.71 (t, 2H, $J = 4.0$ Hz, PCH_2Ph), 1.74 (s, 18H, *o*-*t* Bu), 1.49 (s, 18H, *o*-*t*Bu), 1.35 (s, 18H, *p*-*t*Bu), 0.76 (d, 9H, $^3J_{\text{PH}} = 14.1$ Hz, *PtBu*); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) $\delta = 150.7$ (dd, $^2J_{\text{PC}} = 9.2$ Hz, $^2J_{\text{PC}} = 7.5$ Hz, *ipso*-Mes*), 148.8 (d, $^3J_{\text{PC}} = 10.2$ Hz, *o*-Ph), 145.2 (d, $^5J_{\text{PC}} = 1.9$ Hz, *p*-Mes*), 137.3 (d, $^2J_{\text{PC}} = 10.3$ Hz, *ipso*-Ph), 133.7 (d, $^5J_{\text{PC}} = 5.6$ Hz, *p*-Ph), 129.8 (d, $^3J_{\text{PC}} = 4.7$ Hz, *o*-Mes*), 128.8 (d, $^3J_{\text{PC}} = 1.8$ Hz, *o*-Mes*), 126.2 (d, $^3J_{\text{PC}} = 2.7$ Hz, *m*-Ph), 122.8 (d, $^4J_{\text{PC}} = 2.7$ Hz, *m*-Mes*), 120.6 (s, *m*-Mes*), 108.6 (dd, $^1J_{\text{PC}} = 16.8$ Hz, $^1J_{\text{PC}} = 15.8$ Hz, $\text{C}_{\text{sp}2}$), 47.6 (dd, $^1J_{\text{PC}} = 50.6$ Hz, $^3J_{\text{PC}} = 11.6$ Hz, PCMe_3), 38.9 (s, *o*- CMe_3), 37.8 (s, *o*- CMe_3), 37.3 (dd, $^1J_{\text{PC}} = 60.3$ Hz, $^3J_{\text{PC}} = 23.2$ Hz, PCH_2Ph), 35.4 (pseudo-*t*, $^6J_{\text{PC}} = 2.8$ Hz, $^6J_{\text{PC}} = 2.7$ Hz, *p*- CMe_3), 33.8 (s, *o*- CMe_3), 33.7 (s, *o*- CMe_3), 31.9 (s, *p*- CMe_3), 29.6 (pseudo-*t*, $^2J_{\text{PC}} = 3.7$ Hz, $^4J_{\text{PC}} = 3.6$ Hz, PCMe_3); UV–Vis (hexane) λ_{max} (ϵ) = 332 (21400), 383 (16600), 610 (1700); EA Found: C 80.09, H 10.19%, Calc. for $\text{C}_{49}\text{H}_{74}\text{P}_2 \cdot 0.1\text{CHCl}_3$, C 80.02, H 10.13%.

4.3. Thermal reaction of **8**

Diyl **8** (50 mg, 0.069 mmol) was dissolved in toluene (5 mL) and was heated at 100 $^{\circ}\text{C}$ for 3 h. Analysis by ^{31}P NMR indicated that phosphaalkyne **1** was the sole phosphorus product.

4.4. X-ray crystallography

X-ray diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer. The structure

was solved by direct methods (SIR92) [21] and expanded using Fourier techniques (DIRDIF94) [22]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found by difference Fourier synthesis and refined isotropically. Structure solution, refinement, and graphical representation were carried out using the teXsan package [23].

8: $\text{C}_{52}\text{H}_{77}\text{P}_2 \cdot 3\text{CHCl}_3$, $M = 1083.20$, orthorhombic, $P2_12_12_1$ (#19), $a = 17.5373(4)$, $b = 28.7617(6)$, $c = 11.3338(2)$ Å, $V = 5716.8(2)$ Å³, $Z = 4$, $2\theta_{\text{max}} = 55.0^{\circ}$, $T = 130$ K, $\rho = 1.258$ g cm⁻³, $\mu = 0.529$ mm⁻¹, $F(000) = 2288.00$, 40816 collected reflections, 7048 unique reflections ($R_{\text{int}} = 0.053$), $R1 = 0.064$ ($I > 2\sigma I$), $R_w = 0.084$ (all data), $S = 1.63$ (578 parameters), CCDC-242210.

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References

- [1] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, J. Am. Chem. Soc. 103 (1981) 4587; M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, J. Am. Chem. Soc. 104 (1982) 6167.
- [2] G. Märkl, H. Sejpka, Tetrahedron Lett. 27 (1986) 171.
- [3] G. Becker, G. Gresser, W. Uhl, Z. Naturforsch. B 36 (1981) 16.
- [4] M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Georg Thieme Verlag, Stuttgart, 1990.
- [5] K.B. Dillon, F. Mathey, J.F. Nixon, Phosphorus: The Carbon Copy, Wiley, Chichester, 1998.
- [6] S. Ito, H. Sugiyama, M. Yoshifuji, Chem. Commun. (2002) 1744.
- [7] A.M. Arif, A.R. Barron, A.H. Cowley, S.W. Hall, J. Chem. Soc., Chem. Commun. (1988) 171.
- [8] H. Sugiyama, S. Ito, M. Yoshifuji, Angew. Chem., Int. Ed. 42 (2003) 3802.
- [9] (a) E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, W.W. Schoeller, Angew. Chem., Int. Ed. Engl. 34 (1995) 555; (b) E. Niecke, A. Fuchs, M. Nieger, Angew. Chem., Int. Ed. 38 (1999) 3028.
- [10] D. Scheschkewitz, H. Amii, H. Gornitzka, W.W. Schoeller, D. Bourissou, G. Bertrand, Science 295 (2002) 1880.
- [11] W.W. Schoeller, C. Begemann, E. Niecke, D. Gudat, J. Phys. Chem. A 105 (2001) 10731.
- [12] (a) H. Grützmacher, F. Brehler, Angew. Chem., Int. Ed. 41 (2002) 4006; (b) C. Wentrup, Science 295 (2002) 1846.
- [13] C.K. Johnson, ORTEPII, Oak Ridge National Laboratory Report, No. ORNL-TM-5138, 1976.
- [14] E. Niecke, A. Fuchs, M. Nieger, O. Schmidt, W.W. Schoeller, Angew. Chem., Int. Ed. 38 (1999) 3031.
- [15] H. Sugiyama, S. Ito, M. Yoshifuji, Chem. Eur. J. 10 (2004) 2700.
- [16] R. Appel, J. Peters, A. Westerhaus, Angew. Chem., Int. Ed. Engl. 21 (1982) 80.
- [17] M.J. Yoshifuji, Synth. Org. Chem. Jpn. 61 (2003) 1116.

- [18] S. Ito, S. Sekiguchi, M. Yoshifuji, *J. Org. Chem.* 69 (2004) 4181.
- [19] S. Ito, H. Sugiyama, M. Yoshifuji, *Angew. Chem., Int. Ed.* 39 (2000) 2781.
- [20] M. Yoshifuji, S. Ito, *Top. Curr. Chem.* 223 (2003) 67.
- [21] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G.J. Polidori, *Appl. Crystallogr.* 27 (1994) 435.
- [22] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The *DIRDIF94* program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
- [23] Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985, 1999.