

153. Homogeneous Catalysis with Dicationic Pd^{II} Complexes: Aldol Reaction of Methyl Isocyanoacetate with Benzaldehyde

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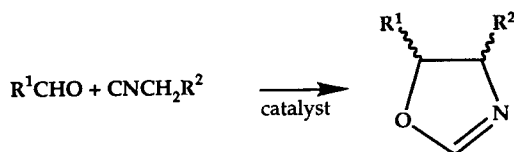
(5. V. 93)

A series of dicationic Pd^{II}-acetonitrile complexes containing bi- and tridentate nitrogen and bidentate phosphine ligands (some of which are chiral) has been prepared as their BF₄ salts. The molecular structures for two of these, [Pd(CH₃CN)₂(bipy)](BF₄)₂ (**4**) and [Pd(CH₃CN)((pybox)(i-Pr))](BF₄)₂((S,S)-pybox(i-Pr) = 2,6-bis[(S)-4'-isopropoxyloxazolin-2'-yl]pyridine, **5**) have been determined by X-ray diffraction. All of these complexes are shown to be effective homogeneous catalysts for the aldol-type condensation of the isonitrile, methyl isocyanoacetate, with benzaldehyde. Two isonitrile complexes, [Pd(2,2'-bipyridyl)(CNCH₂COOCH₃)₂](BF₄)₂ and [Pd((S,S)-pybox(i-Pr))(CNCH₂COOCH₃)₂](BF₄)₂, have also been prepared.

Introduction. – The applications of *Lewis* acids in synthetic chemistry continue to grow. Apart from stoichiometric studies directed towards organic synthesis [1], often with main-group elements [2], transition-metal complexes can be used as *Lewis* acids in several homogeneously catalyzed reactions [3]. In this latter chemistry, it is generally accepted that one or more of the reagents coordinates to the metal center, thereby altering the electronic structure of the substrate and enhancing its reactivity.

We have recently become interested in structural aspects of such transition-metal reagents [4], and specifically [5], the nature of the intermediates in the aldol-type condensation shown in *Scheme 1*. This chemistry has been reported in detail by *Hayashi* and

Scheme 1

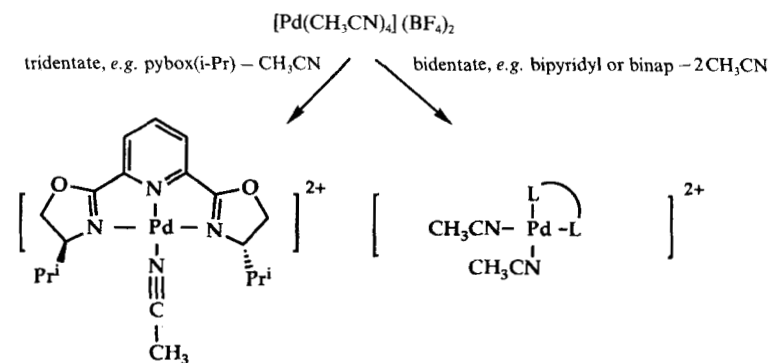


coworkers [6] and refined and extended by *Togni et al.* [7]. The catalyst consists of a labile Au^I complex, *e.g.* [AuCl(Me₂S)], in combination with a chiral ferrocene bis-phosphine ligand. It is assumed that the isonitrile coordinates to the metal *via* the C-atom, and that this coordinated ligand, after deprotonation by a suitable base, is attacked by the aldehyde without this latter reagent ever interacting with the Au^I center. Chiral oxazoline products are obtained, with good-to-excellent optical yields, when the ferrocene phosphine contains a suitable chiral tertiary amine side chain which can also act as a base. It is thought that the deprotonated enolate form of the coordinated isonitrile (*e.g.*, CNCH=C(OMe)O[−] for the enolate with R² = CO₂Me) can interact *via* H-bonding with the chiral side chain, if this latter contains a suitably placed protonated tertiary amine function [6].

Given the increasing number of readily available Pd^{II} salts and our background involving their use [8], we have considered the possible applications of complexes of this less expensive metal as catalyst for the reaction shown in *Scheme 1*. We report here on *a*) the use Pd^{II} dicationic catalysts with respect to the chemistry of *Scheme 1*, *b*) the preparation of several new dicationic Pd^{II} salts, *c*) the isolation of two intermediate structures with coordinated isonitrile ligands, and *d*) the solid-state structures for two catalyst precursors as determined by X-ray diffraction.

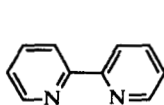
Results and Discussion. – Although one could carry out the catalytic runs by adding a source of Pd^{II} to a ligand followed by addition of the organic substrates, we have elected to prepare and isolate the Pd^{II} precursors separately.

Scheme 2

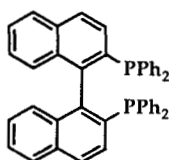


all the complexes as BF₄ salts.

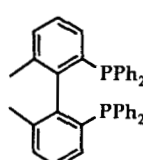
Ligands used in this work



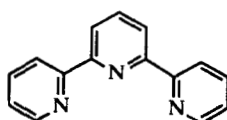
bipyridyl



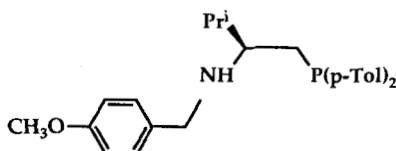
(-)-(R)-binap



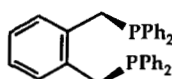
(S)-biphemp



terpyridyl



(-)-(S)-valphos



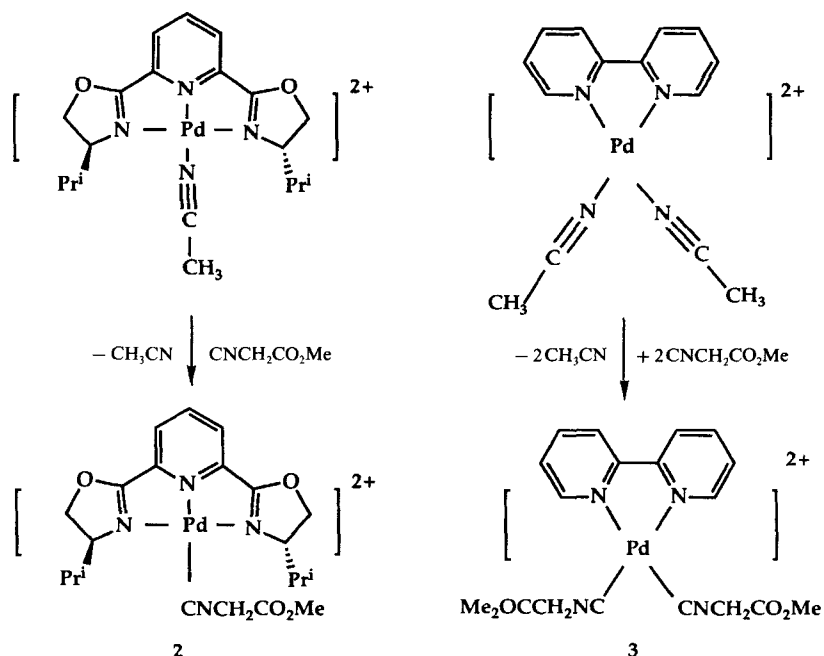
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1. *Synthesis of the Complexes.* All of the dicationic Pd^{II} complexes were prepared from the well-known [9] starting material, $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (**1**) and the appropriate chelate ligand, as shown in *Scheme 2*. We consider here two kinds of complex: those with two coordinated CH_3CN ligands and a nitrogen or phosphorus bidentate ligand, and those with one complexed CH_3CN and a tridentate N-ligand, e.g. pybox(i-Pr) [10], as shown in *Scheme 2*. The isolated yields were good-to-excellent and preparative details are given in *Experimental*.

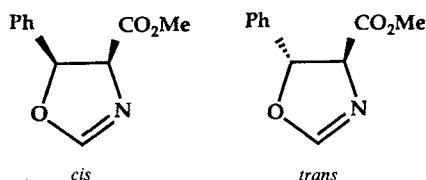
The formulation of these complexes is supported by element analysis and FAB mass spectroscopy combined with ^1H -, ^{13}C -, and ^{31}P -NMR spectroscopy. NMR Parameters for our compounds are also given in *Experimental*; however, we note that, in CH_3NO_2 solution, the ^1H chemical shift of a CH_3CN complexed to Pd^{II} in our molecules falls in the range 1.69–2.83 ppm, and is sometimes relatively broad. CH_3CN has its CH_3 resonance at 1.84 ppm in this solvent.

To determine whether more than one coordinated isonitrile facilitates the reaction, we have also prepared the mono-isonitrile complex **2** which contains pybox(i-Pr), and the bis-isonitrile complex **3**, which has a coordinated bipyridyl. These are shown in *Scheme 3* and were characterized as described above for the CH_3CN complexes.

Scheme 3



2. *Catalysis with the Pd^{II} Dications.* All of our Pd^{II} compounds are good catalysts for the aldol condensation of *Scheme 1*, and our results are summarized in *Table 1*. The experimental conditions are mild and the reaction finished within several hours. Typically, 1 mol-% of the complex, PhCHO and $\text{CNCH}_2\text{CO}_2\text{Me}$ were suspended in CHCl_3 .

Table 1. Aldol Reaction of Benzaldehyde with Methyl Isocyanoacetate Catalyzed by Pd^{II} Complexes

Catalyst	Time	Yield [%]	<i>trans/cis</i> ¹⁾	%ee <i>trans</i> /%ee <i>cis</i> ²⁾
[Pd(CH ₃ CN) ₄](BF ₄) ₂	6 h	90.0	1:0.64	
[Pd(2,2'-Bipyridyl)(CH ₃ CN) ₂](BF ₄) ₂	6 h	91.0	1:0.64	
[Pd(2,2':6,2''-Terpyridin)(CH ₃ CN)](BF ₄) ₂	12 h	90.0	1:0.65	
[Pd(PP)(CH ₃ CN) ₂](BF ₄) ₂	6 h	93.1	1:0.56	
[Pd((<i>S</i>)-biphemp)(CH ₃ CN) ₂](BF ₄) ₂	6 h	93.5	1:0.64	3.0:6.2
[Pd((<i>R</i>)-binap)(CH ₃ CN) ₂](BF ₄) ₂	6 h	99.7	1:0.66	2.1:6.9
[Pd(valphos)(CH ₃ CN) ₂](BF ₄) ₂ ³⁾	6 h	91.0	1:0.58	10.8:11.4
[Pd(valphos) ₂ (CH ₃ CN) ₂](BF ₄) ₂ ⁴⁾	6 h	93.8	1:0.55	10.2:14.4
[Pd((<i>S,S</i>)-pybox(<i>i</i> -Pr))(CH ₃ CN)](BF ₄) ₂	12 h	91.0	1:0.70	1.0:1.7
[Pd((<i>S,S</i>)-pybox(Bz))(CH ₃ CN)](BF ₄) ₂	12 h	91.1	1:0.70	5.6:2.8
[Pt((<i>S,S</i>)-pybox(<i>i</i> -Pr)Cl](OTf)	6 h	94.6 ⁵⁾	1:0.73	4.7:3.1

¹⁾ *cis/trans*-Ratio determined via ¹H-NMR.²⁾ ee Values determined via chiral GC (*Chirasil-L-Val* 50 M, A. Togni, Ciba Geigy, Basel).³⁾ Not characterized. Ligand/Pd 1:1, number of coordinated CH₃CN not determined.⁴⁾ Ligand/Pd 2:1, number of coordinated CH₃CN not determined.⁵⁾ Carried out at room temperature with addition of 1 equiv. of silver triflate.

Addition of Et(*i*-Pr)₂N (10 mol-%) was followed by refluxing for 6 h. After workup of the products the *cis/trans*-dihydrooxazole distribution was assayed via NMR spectroscopy.

We find that the chemical yields are good (generally > 90 %), suggesting that Pd^{II} will be a useful alternative to Au^I and worth future consideration with respect to this C–C bond making reaction. The *trans/cis* ratio at ca. 3:2 is relatively independent of the nature of the accompanying ligand. Indeed, in the absence of a chelating nitrogen or phosphine ligand, *i.e.*, with tetrakis(acetonitrile)palladium(II) tetrafluoroborate, the reaction proceeds just as smoothly and with more or less the same product distribution. With a gold catalyst, the *trans/cis*-ratio is typically [6] [7] in the range of 4–6:1, so that it would seem that Pd^{II} is less selective than Au^I; however, the ligands used with the latter metal are not strictly comparable to ours. In terms of reaction rates, there is a modest difference between the tridentate and bidentate complexes, with the latter somewhat faster than the former. The optical yields, as determined by both NMR and gas chromatographic methods, are negligible and we shall return to possible reasons for this observation after the structural discussion.

3. *X-Ray Structural Studies on [Pd(CH₃CN)₂(bipy)](BF₄)₂ (4) and [Pd(CH₃CN)-pybox(*i*-Pr)](BF₄)₂ (5).* Both complexes were crystallized from a mixture of CH₃CN and Et₂O and their structures determined by X-ray diffraction. ORTEP views of these molecules are shown in Figs. 1 and 2, respectively, and Tables 2 and 3 show a selection of bond lengths and bond angles for these complexes.

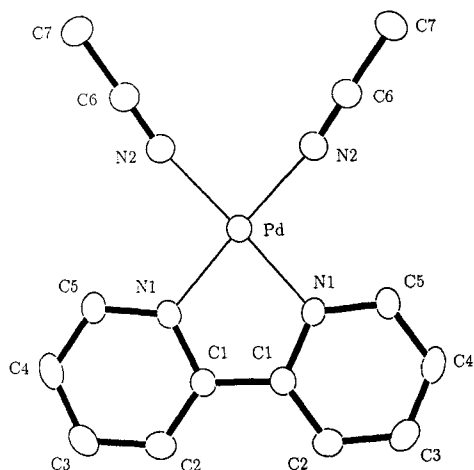


Fig. 1. ORTEP Plot [11] of the molecular structure of **4** (20% probability ellipsoids)

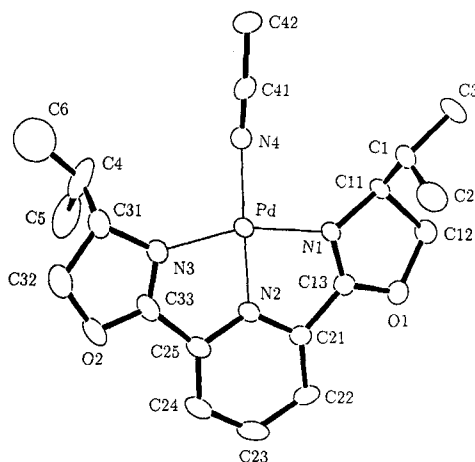


Fig. 2. ORTEP Plot [11] of the molecular structure of **5** (20% probability ellipsoids)

Table 2. Selected Bond Lengths [pm] and Bond Angles [°] for Complex **4**

Bond lengths		Bond angles	
Pd–N(1)	199.2(7)	N(1)–Pd–N(1)	80.9(4)
Pd–N(2)	200.4(8)	N(1)–Pd–N(2)	177.3(3)
N(1)–C(5)	135(2)	N(1)–Pd–N(2)	96.4(3)
N(1)–C(1)	136(1)	N(2)–Pd–N(2)	86.3(5)
C(5)–N(1)	135(2)	N(2)–C(6)–C(7)	178(2)
N(2)–C(6)	111(2)		

Table 3. Selected Bond Lengths [pm] and Bond Angles [°] for Complex **5**

Bond lengths		Bond angles	
Pd–N(2)	192.2(9)	Pd–N(1)	201.7(9)
Pd–N(4)	202.8(9)	Pd–N(3)	203.0(9)
N(1)–C(13)	126(2)	N(1)–C(11)	149(2)
N(2)–C(21)	134(2)	N(2)–C(25)	138(2)
N(3)–C(33)	127(2)	N(3)–C(31)	144(2)
N(4)–C(41)	112(2)	O(1)–C(13)	133(2)
O(1)–C(12)	148(2)	O(2)–C(33)	131(2)
O(2)–C(32)	146(2)	C(11)–C(1)	155(3)
C(11)–C(12)	154(2)		
C(13)–C(21)	148(2)		

In the dication **4**, the coordination geometry is distorted square planar as expected for a d^8 metal center. The coordination angles are normal, with the chelate bite angle, at $80.9(4)^\circ$, in keeping with a five-membered ring. The $N(2)$ –Pd– $N(2)$ angle subtended by the two CH_3CN ligands, at $86.3(5)^\circ$, is only slightly less than the expected 90° value. Interestingly, the Pd– $N(2)$ bond length, 200.4(8) pm, is relatively short, and Table 4

shows this value along with some literature reference data. CH_3CN *trans* to hydride in *trans*- $[\text{PdH}(\text{CH}_3\text{CN})(\text{P}(t\text{-Bu})_3)_2]\text{BF}_4$ [12] has a relatively long Pd–N separation of 212.2(4) pm, and this same bond length for a CH_3CN coordinated to Pd^0 in a butterfly cluster can be comparable [13]. When *trans* to a tertiary phosphine, the corresponding Pd–N distance, 206.5(14) pm, is somewhat shorter [14]. Consequently, our value of 200.8(4) pm is reasonable in that the CH_3CN in **2** is opposite to a ligand of only moderate *trans*-influence [15] relative to H^- or PR_3 and will be more strongly coordinated. It would seem, at least in the ground-state, that the formal 2+ charge on these complexes does not result in a long Pd–N(2) bond.

The $\text{C}\equiv\text{N}$ bond separation, 111.8(12) pm, compares favorably with the unweighted mean found in organic nitriles, 113.6 pm [16], so that there is no major contribution involving π -back bonding from the metal to the nitrile.

The Pd–N separation for the bipyridyl ligand, 199.2(7) pm, falls at the lower end of the expected range for this chelate, see Table 4. It is interesting that for $[\text{Pd}(\text{CN})_2(\text{bipy})]$, the corresponding distance is shorter, 194(1) pm [17], but for $[\text{Pd}(\text{bipy})_2](\text{PF}_6)_2$, the Pd–N separation is longer, 203.9(2) pm [18].

Table 4. Selected Pd–N Bond Lengths [pm] in Pd CH_3CN and Bipyridyl Complexes

Complex	Pd–N(nitrile)	Pd–N(bipyridyl)	Ref.
$[\text{PdH}(\text{CH}_3\text{CN})(\text{P}(t\text{-Bu})_3)_2](\text{BPh}_4)$	212.2(4)		[12]
$[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{CH}_3\text{CN})_2]\text{B}_{10}\text{Br}_{10}$	210(1)		[19]
$[\text{PdCl}_2(\text{CH}_3\text{CN})(\mu\text{-dpmp})\text{PdCl}_2]$	206.5(14) ^{a)}		[14]
$[\text{Pd}_4(\mu\text{-SO}_2)_2(\mu_3\text{-SO}_2)(\text{CH}_3\text{CN})(\text{PPh}_3)_4]$	214(1) ^{b)}		[13]
$[\text{Pd}_2(\text{CH}_3\text{CN})(\text{bipy})(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)]^{2+ c)}$		223.1(2), 217.2(2)	[20]
$[\text{Pd}(\text{bipy})_2](\text{PF}_6)_2$		203.9(2)	[17]
$[\text{Pd}(\text{CN})_2(\text{bipy})]$		194(1)	[16]
$[\text{Pd}(\text{DMSO})\text{Cl}(\text{bipy})]\text{Cl}^d)$		199.6(2) ^{d)}	[21]
$[\text{Pd}(\text{CH}_3\text{CN})_2(\text{bipy})](\text{BF}_4)_2$	200.4(8)	199.2(7)	this work
$[\text{Pd}(\text{CH}_3\text{CN})(\text{pybox}(i\text{-Pr}))(\text{BF}_4)_2]$	202.8(9)		this work

^{a)} P *trans* to CH_3CN .

^{b)} Coordinated to Pd^0 .

^{c)} Acetonitrile Pd–N not given, strained bipy.

^{d)} Shorter Pd–N *trans* to O of DMSO.

The dication **5** contains the chiral tridentate ligand, pybox(*i*-Pr), first prepared by Nishiyama *et al.* [10], who have also reported the crystal structure of $[\text{RhCl}_3(\text{pybox}(i\text{-Pr}))]$ [10]. For both **5** and $[\text{RhCl}_3(\text{pybox}(i\text{-Pr}))]$, the *cis*-N–M–N angles associated with the tridentate are informative in that they are close to 80°. In **5**, these values are 79.5(4)° and 81.8(4)°, for N(1)–Pd–N(2) and N(2)–Pd–N(3), respectively. The N(1)–Pd–N(3) angle of 161.2(4)° confirms that this tridentate ligand leaves a relatively large opening for the complexation of CH_3CN (or $\text{CNCH}_2\text{CO}_2\text{Me}$) in the fourth coordination position. The ORTEP view (Fig. 2) shows this opening quite clearly.

In **5**, the Pd–N bond distance for the nitrile, 202.8(9) pm is, once again, at the lower end of its range, and the $\text{C}\equiv\text{N}$ bond is normal [16] at 112.0(15) pm. The two oxazoline Pd–N separations are somewhat short at 201.7(9) and 202.8(9) pm; however, the pyridine Pd–N bond length is very short, 192.2(9) pm. This is presumably related to the

weak *trans*-influence of the CH_3CN combined with the chelate effect associated with this pyridine-N-atom being the common donor in the two five-membered rings. When *trans* to a tertiary phosphine, the bond between a pyridine-N-atom and Pd^{II} can be *ca.* 215 pm in length [22].

4. *Comments.* The observations that both complex **5** and the terpyridine analog are effective catalysts support the idea that only one coordination site is necessary, as suggested earlier in the gold chemistry. The isonitrile complexes **2** and **3** form relatively quickly, and since the latter complex can be used as a catalyst, it is likely that this is an intermediate. We return now to the low optical yields and consider Fig. 3 which shows **5** viewed from behind and slightly above the coordinated CH_3CN . As may be seen, there is no noticeable crowding so that once the isonitrile coordinates, *e.g.*, as in **2**, the aldehyde should have no difficulty approaching this substrate. In support of this suggestion, we show a section of the ^1H -2D-NOESY spectrum for the isonitrile complex **2** in Fig. 4. We find substantial cross-peaks from *both* of the isopropyl Me groups to the equivalent

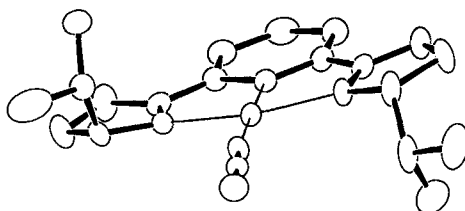


Fig. 3. View of **5** showing the relatively open coordination sphere surrounding the palladium

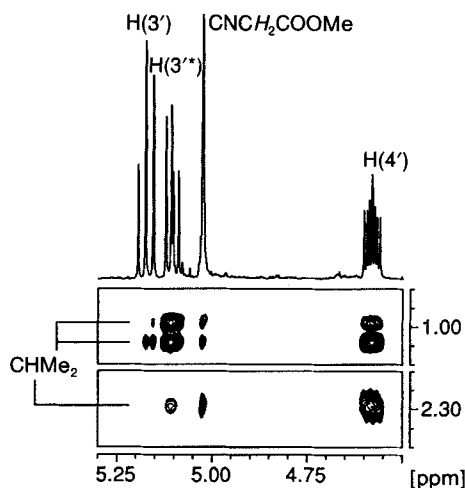


Fig. 4. Section of the 500-MHz ^1H -2D-NOESY spectrum (mixing time = 700 ms, CDCl_3 , ambient temp.) for **2** showing substantial cross-peaks due to NOE's which arise between the $\text{CH}_2\text{CO}_2\text{Me}$, at 5.04 ppm and both the *i*-Pr Me groups, at *ca.* 1 ppm. There is also a cross-peak stemming from the *i*-Pr CH, at *ca.* 2.3 ppm, and H(3'), thereby showing that this latter proton is on the same side of the ring as the *i*-Pr group.

(although potentially diastereotopic) CH_2 protons of the $\text{CH}_2\text{CO}_2\text{Me}$ moiety, *i.e.*, there is no spatial selectivity. We conclude that our chiral pocket is relatively open and does not reach out sufficiently to discriminate between the two enolate faces which exist after deprotonation.

In passing, we note that the use of Pt^{II} instead of Pd^{II} as metal center for the catalysis can significantly accelerate the condensation. Reaction of $[\text{PtCl}_2(\text{NCCH}_3)_2]$ with (*S,S*)-pybox(*i*-Pr) followed by treatment with $\text{Ag}(\text{CF}_3\text{SO}_3)$ generates $[\text{Pt}((\text{S,S})\text{-pybox}(\text{i-Pr}))(\text{NCCH}_3)(\text{CF}_3\text{SO}_3)]$ *in situ* which we used for the catalytic run without further purification. The observed rate increase is, superficially, contrary to the experience of most coordination chemists. Normally, substitution reactions are usually [23] faster for Pd^{II} than Pt^{II} . However, if we assume that Pd^{II} will be more labile than Pt^{II} , and that the catalysis requires *coordinated* isonitrile, then we can accommodate our observation. The Pt-isonitrile complex will be less labile and, therefore, hold the isonitrile longer, thereby accelerating the condensation. We plan to elaborate on this point, together with the applications concerned with tertiary phosphines having polar side chains, later.

Experimental. – General. All reactions were carried out under an inert atmosphere using previously dried solvents. $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ [9], 2,6-bis[(*S*)-4'-isopropylloxazolin-2'-yl]pyridine (= (*S,S*)-pybox(*i*-Pr)) [10], and biphemp [24] were prepared as described in the literature. 1,2-Bis[(diphenylphosphino)methyl]benzene was kindly provided by Prof. L. M. Venanzi. M.p.: uncorrected. IR Spectra: *Perkin-Elmer* 883 spectrophotometer as CsI (or KBr) pills. NMR Spectra: *Bruker AC-250* spectrometer unless otherwise specified. Elemental analyses were determined by the analytical laboratory of the ETH-Zürich.

2,6-Bis[(*S*)-4'-benzyloxazolin-2'-yl]pyridine ((*S,S*)-pybox(*Bz*)). Pyridine-2,6-dicarbonyl chloride (0.866 g, 4.2 mmol) was dissolved in 30 ml of CHCl_3 and slowly treated with a soln. of L-phenylalaninol (1.41 g, 9.3 mmol) in 50 ml of CHCl_3 . After *ca.* 1 min 3.5 ml of Et_3N was added and the resulting soln. stirred for 24 h. Addition of 4 ml of SOCl_2 was followed by refluxing for 2 h. Careful addition of several drops of H_2O preceded addition of 30 ml of 0.1M K_2CO_3 . The org. phase was separated, dried (MgSO_4), and the solvent removed *i.v.* The brownish material which remained was chromatographed using silica gel ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ 2:3) to afford the product as its hydrochloride. Soln. of this compound in 50 ml of MeOH and treatment with 1.1 g of NaOH in 14 ml of H_2O frees the amine. Extraction three times with 50 ml of CH_2Cl_2 was followed by drying the org. phase (MgSO_4). After removal of the solvent, the crude product was washed with 10 ml of MeOH and then recrystallized from $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ to give 1.175 g (70%) of product as colorless crystals. M.p. 156° . $[\alpha]_D^{25} = +36.2$ ($c = 1.0$, CD_3NO_2). IR (KBr): 1634s, 1576s, 1452s, 1131s, 980s, 702s. $^1\text{H-NMR}$ (250 MHz, CDCl_3): 2.74 (*dd*, $J = 13.8, 9.0, 2\text{ H}$); 3.27 (*dd*, $J = 13.8, 5.1, 2\text{ H}$); 4.26 (*dd*, $J = 8.6, 7.6, 2\text{ H}$); 4.46 (*dd*, $J = 9.4, 8.6, 2\text{ H}$); 4.5–4.7 (*m*, 2 H); 7.2–7.4 (*m*, 10 H); 7.90 (*t*, $J = 7.8, 1\text{ H}$); 8.23 (*d*, $J = 7.8, 2\text{ H}$). $^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3): 41.40; 67.82; 72.29; 125.51; 126.30; 128.31; 128.91; 137.03; 137.42; 146.53; 162.44. EI-MS: 397 (8), 306 (100), 214 (10), 145 (12), 117 (21), 91 (39), 84 (15), 31 (30). Anal. calc. for $\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_2$ (397.48): C 75.55, H 5.83, N 10.57; found: C 75.26, H 5.90, N 10.59.

$[\text{Pd}(1,2\text{-Bis}[(\text{diphenylphosphino})\text{methyl}]\text{benzene})(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ (28.0 mg, 0.06 mmol) and 1,2-bis[(diphenylphosphino)methyl]benzene (PP) (29.9 mg, 0.06 mmol) were dissolved in 5 ml of CH_3CN and then stirred at r.t. for 30 min. The soln. was concentrated to *ca.* $\frac{1}{5}$ of its volume and the product precipitated with Et_2O to afford 48.5 mg (92%) of the complex as a pale-yellow solid. M.p. 203° (dec.). IR (CdI): 2323m, 2297m. $^1\text{H-NMR}$ (250 MHz, (D_6)DMSO): 2.08 (*s*, 6 H); 4.48 (*d*, $J(^{31}\text{P}, \text{H}) = 11.7, 4\text{ H}$); 4.4–4.5 (*m*, 2 H); 4.8–5.0 (*m*, 2 H); 7.6–7.9 (*m*, 12 H); 8.0–8.2 (*m*, 8 H). $^{13}\text{C-NMR}$ (62.5 MHz, CD_3NO_2): 2.45; 34.51 ($^1J + ^3J(^{31}\text{P}, ^{13}\text{C}) = 34.8$); 126–136 (*m*). $^{31}\text{P-NMR}$ (101.2 MHz, CD_3NO_2): 22.39. FAB-MS: 599 (6), 580 (12), 475 (4). Anal. calc. for $\text{C}_{36}\text{H}_{34}\text{B}_2\text{F}_8\text{N}_2\text{P}_2\text{Pd}$ (836.30): C 51.70, H 4.07, N 3.35; found: C 51.37, H 4.15, N 3.16.

$[\text{Pd}((\text{S})\text{-biphemp})(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ was prepared as described above. $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (16.4 mg, 0.04 mmol) and (*S*)-biphemp (20.3 mg, 0.04 mmol) in 5 ml of CH_3OH gave 28.2 mg (95%) of product as a yellow solid. M.p. 215° (dec.). $[\alpha]_D^{25} = +204.7$ ($c = 1.00$, CD_3NO_2). IR (CsI): 2320m, 2290m. $^1\text{H-NMR}$ (250 MHz, CD_3NO_2): 1.69 (*s*, 6 H); 1.84 (*s*, 6 H); 7.1–8.0 (*m*, 26 H). $^{13}\text{C-NMR}$ (62.5 MHz, CD_3NO_2): 1.89; 20.33; 120–143 (*m*). $^{31}\text{P-NMR}$ (101.2 MHz, CD_3NO_2): 31.49. FAB-MS: 675 (6), 656 (13), 549 (2). Anal. calc. for $\text{C}_{42}\text{H}_{38}\text{B}_2\text{F}_8\text{N}_2\text{P}_2\text{Pd}$ (912.74): C 55.27, H 4.20, N 7.80; found: C 54.49, H 4.18, N 2.67.

$[\text{Pd}((\text{R})\text{-binap})(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ was prepared as described above. $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (53.6 mg, 0.12 mmol) and (*R*)-binap (75.2 mg, 0.12 mmol) in 5 ml of CH_3CN gave 117.6 mg (98%) of product as a yellow powder.

M.p. 198° (dec.). $[\alpha]_D^{25} = +510.8$ ($c = 1.00$, CD_3NO_2). IR (CsI): 2325 m , 2301 m . $^1\text{H-NMR}$ (250 MHz, CD_3NO_2): 1.90 (s , 6 H); 6.7–8.0 (m , 32 H). $^{13}\text{C-NMR}$ (62.5 MHz, CD_3NO_2): 2.08; 119–142 (m). $^{31}\text{P-NMR}$ (101.2 MHz, CD_3NO_2): 30.40. FAB-MS: 747 (5), 728 (13), 621 (2). Anal. calc. for $\text{C}_{48}\text{H}_{38}\text{B}_2\text{F}_8\text{N}_2\text{P}_2\text{Pd}$ (984.40): C 58.54, H 3.89, N 2.84; found: C 57.26, H 4.06, N 2.63.

$[\text{Pd}(2,2'\text{-Bipyridyl})(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ was prepared as described above. $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (115.0 mg, 0.26 mmol) and 2,2'-bipyridyl (40.5 mg, 0.26 mmol) in 5 ml of CH_3CN gave 126.2 mg (94%) of product as a pale-yellow solid. Crystals suitable for X-ray diffraction were obtained from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$. M.p. 256° (dec.). IR (CsI): 2332 m , 2303 m . $^1\text{H-NMR}$ (250 MHz, CD_3NO_2): 2.75 ($br.$, 6 H); 7.84 (t^* , $J = 6.5$, 2 H); 8.3–8.5 (m , 4 H); 8.60 (d^* , $J = 5.2$, 2 H). $^{13}\text{C-NMR}$ (62.9 MHz, CD_3NO_2): 4.01; 126.05; 126.44; 130.03; 145.18; 153.54; 158.57. FAB-MS: 262 (42), 157 (44). Anal. calc. for $\text{C}_{14}\text{H}_{14}\text{B}_2\text{F}_8\text{N}_4\text{Pd}$ (518.31): C 32.44, H 2.72, N 10.81; found: C 32.18, H 2.54, N 10.92.

$[\text{Pd}(2,2':6',2''\text{-Terpyridine})(\text{CH}_3\text{CN})](\text{BF}_4)_2$ was prepared as described above. $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (356.6 mg, 0.80 mmol) and 2,2':6',2''-terpyridine (187.4 mg, 0.80 mmol) in 15 ml of CH_3CN gave 425.6 mg (96%) of product as a pale-yellow solid. M.p. > 280° (dec.). $^1\text{H-NMR}$ (250 MHz, CD_3NO_2): 2.83 ($br.$, 3 H); 7.92 (t , $J = 6.5$, 2 H); 8.4–8.8 (m , 9 H). $^{13}\text{C-NMR}$ (62.9 MHz, CD_3NO_2): 4.02; 125.97; 126.87; 127.04; 130.85; 144.94; 145.89; 154.31; 157.74; 158.95. FAB-MS: 358 (25), 339 (74), 234 (11). Anal. calc. for $\text{C}_{17}\text{H}_{14}\text{B}_2\text{F}_8\text{N}_4\text{Pd}$ (554.34): C 36.83, H 2.55, N 10.11; found: C 37.07, H 2.58, N 10.24.

$[\text{Pd}((S,S)\text{-pybox}(i\text{-Pr}))(\text{CH}_3\text{CN})](\text{BF}_4)_2$ was prepared as described above. $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (55.3 mg, 0.13 mmol) and (S,S) -pybox($i\text{-Pr}$) (37.5 mg, 0.13 mmol) in 5 ml of CH_3CN gave 73.1 mg (94%) of product as a yellow solid. Crystals suitable for X-ray diffraction were obtained from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$. M.p. 246° (dec.). $[\alpha]_D^{25} = +183.2$ ($c = 1.01$, CD_3NO_2). IR (CsI): 2332 m , 2306 m . $^1\text{H-NMR}$ (250 MHz, CD_3NO_2): 1.02 (d , $J = 2.8$, 6 H); 1.05 (d , $J = 3.0$, 6 H); 2.2–2.3 (m , 2 H); 4.56 (ddd , $J = 10.1$, 9.6, 6.9, 2 H); 5.08 (dd , $J = 9.6$, 6.9, 2 H); 5.16 (dd , $J = 10.1$, 9.6, 2 H); 8.20 (d , $J = 8.0$, 2 H); 8.70 (t , $J = 8.0$, 1 H). $^{13}\text{C-NMR}$ (62.9 MHz, CD_3NO_2): 3.69; 15.25; 18.59; 31.57; 69.25; 76.05; 128.64; 130.16; 146.65; 147.68; 171.95. FAB-MS: 426 (77), 407 (100), 302 (7). Anal. calc. for $\text{C}_{19}\text{H}_{26}\text{B}_2\text{F}_8\text{N}_4\text{O}_2\text{Pd}$ (622.45): C 36.66, H 4.21, N 9.00; found: C 36.78, H 4.27, N 8.94.

$[\text{Pd}((S,S)\text{-pybox}(\text{Bz}))(\text{CH}_3\text{CN})](\text{BF}_4)_2$ was prepared as described above. $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (45.4 mg, 0.10 mmol) and (S,S) -pybox(Bz) (40.6 mg, 0.10 mmol) in 5 ml of CH_3CN gave 71.3 mg (96%) of product as a yellow solid. M.p. 152° (dec.). $[\alpha]_D^{25} = +262.8$ ($c = 0.99$, CD_3NO_2). IR (CsI): 2332 m , 2306 m . $^1\text{H-NMR}$ (250 MHz, CD_3NO_2): 2.53 ($br.$, 3 H); 3.06 (dd , $J = 14.1$, 6.9, 2 H); 3.18 (dd , $J = 14.1$, 6.1, 2 H); 4.7–4.9 (m , 2 H); 5.01 (dd , $J = 9.4$, 5.6, 2 H); 5.13 (t , $J = 9.5$, 2 H); 7.2–7.5 (m , 10 H); 8.11 (d , $J = 8.1$, 2 H); 8.63 (t , $J = 8.1$, 1 H). $^{13}\text{C-NMR}$ (62.9 MHz, CD_3NO_2): 4.08; 40.59; 65.08; 79.42; 127.59; 128.86; 129.97; 130.44; 131.26; 136.14; 146.67; 147.70; 172.30. FAB-MS: 522 (80), 503 (100), 398 (7). Anal. calc. for $\text{C}_{27}\text{H}_{26}\text{B}_2\text{F}_8\text{N}_4\text{O}_2\text{Pd}$ (718.54): C 45.13, H 3.65, N 7.80; found: C 44.92, H 3.96, N 7.57.

$[\text{Pd}(2,2'\text{-Bipyridyl})(\text{NCCH}_2\text{COOCH}_3)_2](\text{BF}_4)_2$. $[\text{Pd}(2,2'\text{-Bipyridyl})(\text{NCCH}_3)_2](\text{BF}_4)_2$ (81.3 mg, 0.157 mmol) and 28.5 ml (0.314 mmol) of methyl isocyanoacetate were stirred at r.t. in 5 ml of CH_3CN for 10 min. The soln. was concentrated to ca. 1 ml and the product precipitated with Et_2O to afford 103.0 mg (99%) of a yellow-green solid. M.p. 192° (dec.). IR (CsI): 2320 w , 2253 s , 1765 s , 1753 s . $^1\text{H-NMR}$ (250 MHz, CD_3NO_2): 3.95 (s , 3 H); 5.18 (s , 2 H); 7.93 (t , $J = 5.7$, 2 H); 8.52–8.54 (m , 2 H); 8.55 (d , $J = 1.1$, 2 H); 9.05 (d , $J = 5.5$, 2 H). $^{13}\text{C-NMR}$ (62.9 MHz, CD_3NO_2): 48.54 ($J(^{14}\text{N}, ^{13}\text{C}) = 17.9$); 55.15; 116.82 ($J(^{14}\text{N}, ^{13}\text{C}) = 55.8$); 117.25; 126.25; 130.52; 145.19; 155.85; 158.36; 164.97. FAB-MS: 477 (8), 361 (13), 262 (16), 157 (24). Anal. calc. for $\text{C}_{18}\text{H}_{18}\text{B}_2\text{F}_8\text{N}_4\text{O}_4\text{Pd}$ (634.38): C 34.08, H 2.86, N 8.83; found: C 34.02, H 2.79, N 8.95.

$[\text{Pd}((S,S)\text{-pybox}(i\text{-Pr}))(\text{NCCH}_2\text{COOCH}_3)](\text{BF}_4)_2$ was prepared as described above for $[\text{Pd}(2,2'\text{-Bipyridyl})(\text{NCCH}_2\text{COOCH}_3)_2](\text{BF}_4)_2$. $[\text{Pd}((S,S)\text{-pybox}(i\text{-Pr}))(\text{NCCH}_3)](\text{BF}_4)_2$ (104.7 mg, 0.168 mmol) and 15.3 ml (0.168 mmol) of methyl isocyanoacetate in 5 ml of CHCl_3 gave 106.8 mg (93%) of product as a yellow-green solid. M.p. 187° (dec.). IR (CsI): 2279 m , 1758 s . $^1\text{H-NMR}$ (250 MHz, CD_3NO_2): 1.00 (d , $J = 6.8$, 6 H); 1.05 (d , $J = 7.0$, 6 H); 2.1–2.4 (m , 2 H); 3.91 (s , 3 H); 4.59 (ddd , $J = 10.2$, 7.1, 3.9, 2 H); 5.04 (s , 2 H); 5.11 (dd , $J = 9.7$, 7.1, 2 H); 5.19 (dd , $J = 10.2$, 9.7, 2 H); 8.28 (d , $J = 8.1$, 2 H); 8.74 (t , $J = 8.1$, 1 H). $^{13}\text{C-NMR}$ (62.9 MHz, CD_3NO_2): 14.89; 18.66; 31.73; 48.19 ($J(^{14}\text{N}, ^{13}\text{C}) = 16.8$); 55.02; 69.82; 76.06; 118.96 ($J(^{14}\text{N}, ^{13}\text{C}) = 50.5$); 130.23; 145.93; 148.14; 164.92; 173.05. MS (FAB): 523 (19), 506 (22), 426 (50), 407 (100), 302 (10). Anal. calc. for $\text{C}_{21}\text{H}_{28}\text{B}_2\text{F}_8\text{N}_4\text{O}_4\text{Pd}$ (680.49): C 37.07, H 4.15, N 8.23; found: C 37.03, H 4.20, N 8.18.

$[\text{Pt}((S,S)\text{-pybox}(i\text{-Pr}))\text{Cl}](\text{CF}_3\text{SO}_3)_2$. $\text{PtCl}_2(\text{NCCH}_3)_2$ (196.1 mg, 0.56 mmol), (S,S) -pybox($i\text{-Pr}$) (169.8 mg, 0.56 mmol) and silver trifluoromethanesulfonate (144.8 mg, 0.56 mmol) were dissolved in 100 ml of acetone and then refluxed for 15 h. Filtration through *Celite* and solvent removal *i.v.* was followed by recrystallization from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ to afford 318.2 mg (83%) of product as orange crystals. M.p. 210° (dec.). $[\alpha]_D^{25} = +212.5$ ($c = 1.00$, CD_3NO_2). IR (CsI): 347 m . $^1\text{H-NMR}$ (250 MHz, CD_3OD): 0.93 (d , $J = 6.9$, 6 H); 0.99 (d , $J = 7.1$, 6 H); 2.5–2.8 (m , 2 H); 4.44 (ddd , $J = 10.0$, 7.9, 3.6, 2 H); 5.1–5.2 (m , 4 H); 8.14 (d , $J = 8.1$, 2 H); 8.57 (d , $J = 8.1$, 1 H). $^{13}\text{C-NMR}$ (62.9 MHz, CD_3OD): 14.20; 18.61; 30.03; 69.35 ($J(^{195}\text{Pt}, ^{13}\text{C}) = 43.1$); 75.49 ($J(^{195}\text{Pt}, ^{13}\text{C}) = 24.3$); 128.90

($J(^{195}\text{Pt}, ^{13}\text{C}) = 30.5$); 143.94; 146.21; 175.80. FAB-MS: 645 (33), 532 (100), 496 (15), 302 (6). Anal. calc. for $\text{C}_{18}\text{H}_{23}\text{ClF}_3\text{N}_3\text{O}_5\text{SPt}$ (681.00): C 31.75, H 3.40, N 6.17; found: C 31.97, H 3.56, N 6.30.

Typical Catalytic Run. To $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (34.5 mg, $7.8 \cdot 10^{-5}$ mol) as a suspension in 5 ml of CHCl_3 were added 0.78 ml ($7.8 \cdot 10^{-3}$ mol) benzaldehyd, 0.78 ml ($8.5 \cdot 10^{-3}$ mol) methyl isocyanoacetate, and 0.07 ml ($7.8 \cdot 10^{-4}$ mol) $\text{Et}(\text{i-Pr})_2\text{N}$. After refluxing for 6 h, the solvent and other volatiles were removed and the residue extracted with 3×10 ml portions of Et_2O . After distillation of Et_2O *i.v.*, the brown oil which remained was subjected to a bulb-to-bulb distillation. The product 4-(methoxycarbonyl)-5-phenyl-2-oxazoline (1.49 g, 90%) is a colorless oil and reveals a *trans/cis*-ratio of 1:0.64. *trans*-Isomer: $^1\text{H-NMR}$ (250 MHz, CDCl_3): 3.78 (s, 3 H); 4.61 (dd, $J = 7.2, 2.2$, 1 H); 5.68 (d, $J = 7.7$, 1 H); 7.08 (d, $J = 2.2$, 1 H); 7.2–7.4 (m, 5 H). $^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3): 52.82; 75.32; 82.08; 125.57; 128.76; 128.94; 138.95; 156.33; 170.86. *cis*-Isomer: $^1\text{H-NMR}$ (250 MHz, CDCl_3): 3.19 (s, 3 H); 5.09 (dd, $J = 11.1, 2.0$, 1 H); 5.74 (d, $J = 11.1$, 1 H); 7.2–7.4 (m, 6 H). $^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3): 51.64; 72.53; 81.87; 126.27; 128.23; 128.71; 135.96; 157.46; 168.94.

X-Ray Diffraction. Crystals of **4** and **5** were selected and prepared under a microscope with polarized light. Diffraction data were collected with MoK_α radiation ($\lambda = 71.073$ pm, graphite monochromator on a *Stoe STADI4* diffractometer) up to $\sin\theta/\lambda = 0.65 \cdot 10^{-2} \text{ pm}^{-1}$ using ω - 2θ scan mode. The space group determination for compound **4** is consistent with $P2_1/m$ or $P2_1$. Due to the occurrence of strong correlations during the refinement in the noncentrosymmetric space group $P2_1$, the centrosymmetric space group $P2_1/m$ was chosen. The acentric space group $P2_12_12_1$ for **5** is unambiguously determined from systematic absences. The absolute configuration is determined by the use of optically pure starting materials.

The structures were solved by Patterson methods [25] and refined by full-matrix least-squares on F [26] with 150 free parameters for **4** (an overdetermination factor of 12) and 329 free parameters for **5** (an overdetermination factor of 6). Crystal data are given in Table 5, whereas selected bond lengths and angles in Tables 2 and 3. The

Table 5. Crystal Data for **4** and **5**

	4	5
Formula	$\text{C}_{14}\text{H}_{14}\text{B}_2\text{F}_8\text{N}_4\text{Pd}$	$\text{C}_{19}\text{H}_{26}\text{B}_2\text{F}_8\text{N}_4\text{O}_2\text{Pd}$
Unit cell	$a = 877.3(2)$ pm $b = 1206.1(3)$ pm $c = 918.8(2)$ pm $\beta = 99.21(2)^\circ$	$a = 1216.9(2)$ pm $b = 1787.8(2)$ pm $c = 1189.4(3)$ pm
Space group	$P2_1/m$ C_{2h}^2 (No. 11)	$P2_12_12_1$ D_{2d}^5 (No. 19)
Volume [$10^6 \cdot \text{pm}^3$]	959.7(4)	2587.6(9)
Formula units per cell	2	4
Mol. wt. [$\text{g} \cdot \text{mol}^{-1}$]	518.3	622.44
Density _{calc.} [$\text{g} \cdot \text{cm}^{-3}$]	1.7907	1.5978
μ (MoK_α) [cm^{-1}]	9.37	7.08
Absorption correction	empirical (Ψ -scan)	empirical (Ψ -scan)
Min./max. transmission factors	0.7352/0.8115	0.851/0.9997
Min./max. 2θ	$3^\circ \leq 2\theta \leq 55^\circ$	$3^\circ \leq 2\theta \leq 55^\circ$
No. of measured reflections	2330	3356
No. of reflections with $F^2 > 3\sigma F^2$	1804	2044
$R(\text{aniso})^a$	0.064	0.043
$R_w(\text{aniso})^b$	0.066	0.042

$$^a) R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}, \quad ^b) R = \frac{\sum (|F_o| - |F_c| \sqrt{w})}{\sum |F_o|}, \quad w = \frac{k}{\sigma^2 \cdot |F_o| + |g| \cdot |F_o|^2}.$$

H-positions were included at calculated sites with fixed isotropic thermal parameters and allowed to ride on the bonded C-atom. All other atoms were refined anisotropically except the B-atoms of **4** because of large displacements and/or static disorder for the BF_4^- groups. Thus, all F-atoms of the BF_4^- anions were constrained to a B–F bond length of 137 pm and an F–F distance of 223.7 pm to form rigid group tetrahedrons. The disorder observed for the BF_4^- group proximate to i-Pr group C(4), C(5), C(6) (*cf.* Fig. 1) is especially reflected by the anisotropic temp. ellipsoids of the i-Pr group in **5**.

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