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Synthesis and characterization of a planar chiral and chiral-at-metal ruthenium *N*-heterocyclic carbene complex

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Abstract

This report describes the conversion of the neutral planar chiral arene-tethered complex [Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4PCy_2$)Cl_2 (**1**), into [Ru(η^6: η^1-$Me_2NC_6H_4C_6H_4PCy_2$)(1,3-dibutylimidazol-2-ylidene)Cl]BF_4 (**2**) *via* silver transmetallation. The cationic title complex is also chiral-at-metal, and forms stereoselectively as a result of the directing effect of the arene-tethered ligand. The structure in solution and in the solid state was examined; a puckered distortion of the η^6-arene was noted in the crystal structure, along with a hindered rotation of the NHC in solution. As a comparison to the previously reported phosphine analogues, the dication derived from **2** was used to catalyze the asymmetric Diels-Alder reaction of methacrolein and cyclopentadiene.

Keywords: Metal-centered chirality; Catalysis; Carbene; Ring slip; Tether; Fluxional

1. Introduction

With the recent emergence of *N*-heterocyclic carbenes (NHC's) as ancillary ligands for organometallic complexes, much focus has been given to novel preparations and utilities of NHC complexes. The strong σ-donating capability and unique steric geometry of NHC ligands makes them attractive alternatives to phosphines as spectator ligands for catalytic reactions [1,2]. Not only are transition metal NHC complexes often quite robust, they can also impart distinctive steric and electronic properties to transition metal complexes [3]. Not surprisingly, their impact in catalysis has been enormous, perhaps most notably in the areas of Ru catalyzed olefin metathesis reactions [4,5], and Pd catalyzed cross coupling reactions [6–9]. Their influence in arene ruthenium chemistry has also been noteworthy; such complexes containing NHC ligands have found recent catalytic applications for the polymerization [10], metathesis [11–15], and cycloisomerization [13,14] of olefins, the synthesis of furans [16–19], the hydrogenation of alkenes [20], and for cyclopropanation reactions [21].

This report details the conversion of the neutral planar chiral arene-tethered ruthenium complex Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4PCy_2$)Cl_2 (**1**) into a cationic NHC analogue [Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4PCy_2$)(1,3-dibutylimidazol-2-ylidene)Cl]BF_4 (**2**), *via* a silver transmetallation route. The resulting cationic NHC complex is both planar chiral and chiral-at-metal, and is part of our ongoing examination on the effect of metal-centered chirality in asymmetric catalysis. This synthesis is diastereoselective and furnishes a single isomer of **2**, the stereochemistry of which was confirmed with X-ray crystallography. Since **1** can be conveniently resolved by conversion to a BINAM derivative [22], enantiomerically pure samples of 2 can also be obtained. In addition to examining its solution dynamics, **2** was also shown to provide a catalyst precursor for the asymmetric Diels-Alder reaction of methacrolein and cyclopentadiene.

2. Results and discussion

The silver transmetallation protocol developed by Lin and Wang has become a powerful method for the

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preparation of transition metal NHC complexes [23,24]. These silver transfer agents have been successfully applied to the synthesis of NHC complexes of a variety of transition metals, notably Au, Pd, Pt, Rh, Ir, and Cu [24]. Thus far, however, silver transmetallations to Ru have been comparatively rare [25,26], despite the enormous success in catalysis achieved with Ru–NHC complexes. In particular, the preparation of half-sandwich complexes of the type [Ru(η^6-arene)(L)(NHC)Cl]X, where L is a neutral ligand and X is a counterion, *via* silver transmetallation has not, to our knowledge, been reported. Although the syntheses of neutral complexes of the type Ru(η^6-arene)(NHC)Cl_2 have been reported by a number of groups, the derivatization of a neutral ruthenium arene into a cationic NHC complex can be a more difficult task. Specifically, the neutral species Ru(η^6-arene)(L)Cl_2 are generally converted to their cationic analogues by the addition of a silver salt (AgX, where X is a non-coordinating anion), which abstracts a halide ligand from the metal, in the presence of the desired neutral ligand. These silver salts are especially useful in cases where the low lability of the anionic halide ligand precludes its direct displacement by a neutral ligand.

The synthesis of **2** is shown in Fig. 1; a necessary feature of this reaction is the anion exchange which substitutes the non-coordinating anion BF_4^- for Br^-. This type of anion exchange has been used previously by Slaughter and coworkers for the synthesis of a cationic rhodium complex with a chelating bis-NHC ligand [27]. The successful transmetallation of a silver-NHC to another transition metal involves the formation of a silver salt. As most silver halides are quite insoluble in organic solvents, the formation of the desired product is usually accompanied by the precipitation of one of these salts. However, when X is a noncoordinating anion such as BF_4, the salt can potentially remain in solution and therefore can participate in a subsequent reaction. When adding the silver-NHC, then, to a neutral metal halide complex that is substitutionally inert, it is best to use a non-coordinating anion because this will produce a silver salt that will likely affect the abstraction of the halide from the metal. This opens a coordination site for the NHC, and in this case has the same net effect as adding $AgBF_4$ and the free NHC to the neutral species **1**.

The resulting cationic complex, [Ru(η^6:η^1-$Me_2NC_6H_4$-$C_6H_4PCy_2$)(1,3-dibutylimidazol-2-ylidene)Cl]BF_4 (**2**) is an air-stable yellow solid which can be handled in undried solvents for extended periods and chromatographed on silica gel. Importantly, this synthesis is diastereoselective, and only a single isomer is formed. The stereochemistry was confirmed by X-ray crystallography (Fig. 2); as with phosphine analogues that show a similar preference, it is the *anti* isomer that is formed. The *anti* descriptor refers to the position of the NHC with respect to the NMe_2 group. This preference, which has been shown to be both a kinetic and thermodynamic effect, has been attributed to the directing affect of the NMe_2 group [28]. While the lability of certain phosphines has been demonstrated by their relatively slow equilibration, one might expect the NHC analogue to be non-labile owing to the strength of metal–carbene bonds, which tends to prevent their dissociation. Indeed, in this case no equilibration among the *anti* and *syn* isomers was noted in solution, so the diastereoselectivity appears to be a kinetic effect.

An interesting feature of the crystal structure is the planarity of the NMe_2 group, which is a feature that is common to the cationic and dicationic variants of this arene-tethered system [22,28], and is suggestive of an sp^2 hybridization of the N atom. The metrical data is shown

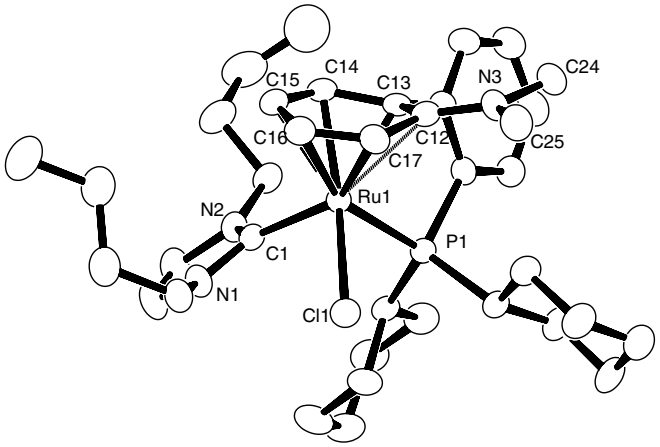

Fig. 2. ORTEP diagram of the cation in S_{Ru}, R-2.

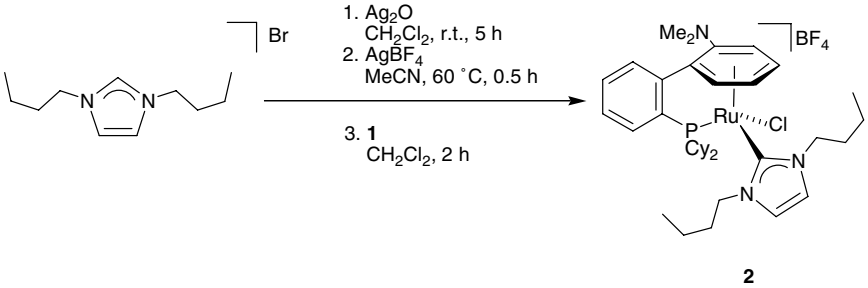

Fig. 1. Synthesis of **2**.

Table 1
Selected bond lengths and angles for **2**

Bond lengths (Å)			
Ru–C1	2.084(2)	Ru–C12	2.466(2)
Ru–P1	2.3361(7)	Ru–C13	2.137(2)
Ru–Cl1	2.4348(6)	Ru–C14	2.161(2)
N3–C12	1.356(3)	Ru–C15	2.246(3)
N3–C24	1.461(3)	Ru–C16	2.239(3)
N3–C25	1.457(3)	Ru–C17	2.279(2)
Torsion angles (°)			
C12–C13–C14–C15	−16.0(3)		
C13–C14–C15–C16	−1.9(4)		
C14–C15–C16–C17	7.4(4)		
C16–C17–C12–C13	22.7(4)		
C13–C12–N3–C24	5.7(4)		
C17–C12–N3–C25	0.4(4)		
Bond angles (°)			
C12–N3–C24	125.1		
C12–N3–C25	119.0		
C24–N3–C25	115.8		

in Table 1. Indeed, the bond angles about that nitrogen atom in **2** are ~116–125°, while for neutral **1** they are ~110–114°. This is likely an effect of the positive charge on the metal, which causes the η^6-ring to be more electron deficient and results in the delocalization of the amino lone pair into the ring. Also noteworthy is the pronounced pucker of the η^6-ring, specifically, the NMe_2-substituted carbon is not coplanar with the remaining portion of the ring. This is evident from the long bond length from the metal to the NMe_2-substituted carbon (2.47 Å, this bond is shown in light gray in Fig. 2), whereas the other ruthenium to η^6-carbon distances range from 2.13 to 2.25 Å. This bond distance (Ru–C12) is larger than what has previously been observed for the cationic and dicationic phosphine and amine complexes. Also, while some of the torsion angles for the η^6-ring are small (e.g. C13–C14–C15–C16 = 1.9°), there are two very large torsion angles of 22.7° and 16.0°, respectively, that illustrate the puckered nature of the ring. The arene carbon attached to nitrogen (C12) is also 0.31 Å out of the mean plane of the remaining arene carbons. In effect, one might consider that the arene may have a large resonance contribution of a zwitterion with a positive nitrogen atom and an η^5-arene anion. The elongation of this Ru–C bond and the pucker effect could be related to the strong *trans* influence of the NHC ligand.

There are two distinct fluxional processes that are observed *via* NMR. That the solid-state structure is not rigidly retained in solution is indicated by the room temperature ^1H and ^{13}C NMR spectra of **2**, each showing a single broad resonance corresponding to the two methyl groups of the NMe_2 moiety. Therefore, a fluxional process that exchanges the two methyl groups is incompletely averaged at room temperature. Indeed, warming to 55 °C sharpened this resonance in the ^1H NMR, although the spectrum was not yet in the fast exchange limit. A low temperature limiting spectrum was obtained by cooling to −40 °C, which now showed two sharp diastereotopic methyl group resonances at 2.87 and 2.57 δ. These resonances initially broadened at −30 °C, suggesting a free energy of activation of ~13 kcal/mol for this process. For the methyl groups to be exchanged through equivalent sites, an umbrella-flip of a pyramidal amine intermediate, a bond rotation of the N–C bond of the arene ring (Fig. 3) or both processes may occur. This observation of a relatively low barrier would not be expected owing to the postulated C=N double bond character suggested by the crystal structure. Thus, in order to accommodate the observed exchange, there should be a decrease in bond order of the C–N bond and possibly the planarity of the NMe_2 group. Nonetheless, the observance of the planar amine, as well as the pucker of the η^6-ring in the solid state, suggests that a similar structure should dominate in solution.

The presence of a high degree of C=N character, however, is contrary to the observation of a low barrier to C–N rotation. This suggests that an intermediate must be accessible that would allow facile rotation about the C–N bond. It is possible that the η^6-ring could be prone to conversion to a lower hapticity, a feature that could, in principle, be exploited for the generation of binding sites that would facilitate a catalytic process. For example, we have recently found a catalytic hydrogenation reaction catalyzed by a coordinatively saturated arene-tethered complex which presumably opens coordination sites by ring slippage [29]. The strong donor character of the carbene may thus facilitate further ring slip in **2**, producing an η^2-, or η^4-intermediate with much more pronounced C–N single bond character thereby lowering the barrier to exchange of the methyl groups.

The other fluxional process involves a higher energy barrier, as indicated by the room temperature ^1H and ^{13}C NMR spectra that show the non-equivalency of the two sides of the NHC ligand. Each of the *n*-butyl groups are diastereotopic (yielding 12 different methylene proton shifts). The protons at the C4 and C5 positions of the NHC are also nonequivalent. These observations are indicative of hindered rotation about the Ru–C bond, which has been observed for other transition metal NHC complexes [30,31], and has been ascribed to a steric barrier to rotation. In this case, warming to 55 °C caused a broadening of the two NHC backbone resonances, along with the resonances correlating to the *n*-butyl groups. The line broadening of

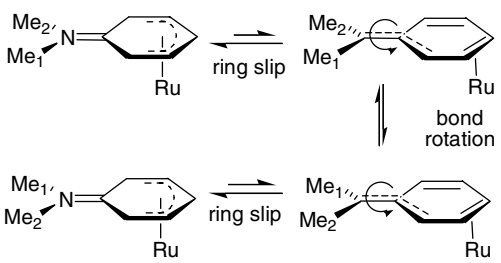

Fig. 3. A mechanism allowing facile averaging of methyl groups in the NMe_2 group. A decrease in hapticity (η^2 is shown) lowers the CN bond order.

the C4 and C5 proton resonances was used to determine a rotation barrier of 17.4 kcal/mol for the NHC in **2**. While the rate of rotation is slow on the NMR timescale, it is still fast relative to a typical reaction rate. However, as *n*-butyl groups are relatively small wingtips, this rotational barrier would likely be increased with bulkier groups. The possibility also remains for the inclusion of an additional element of chirality that would result from the hindered rotation of an NHC with two inequivalent wingtips. The ^{1}H NMR spectrum suggests that the environments of the two *n*-butyl wingtips may in fact be quite different, as two of the diastereotopic methylene protons attached to the same carbon are significantly shifted downfield (at 4.76 and 4.26 δ) with respect to the remaining butyl resonances. That these two protons were attached to the same carbon was verified with a ^{1}H–^{13}C HMQC experiment.

As has been previously mentioned, no epimerization of the metal center in **2** was observed during any of the manipulations carried out in this study, demonstrating the non-labile nature of the NHC ligand. However, epimerization can still be a problem in a catalytic process, since this would require the loss of a ligand, and the inversion barriers for 16 electron metal centers is believed to be comparatively low. Our prior work with phosphine analogues has suggested that the epimerization of the active Lewis acid catalyst for the Diels-Alder reaction of methacrolein and cyclopentadiene was >15 kcal/mol, although the catalyses were still done with equilibrium mixtures of isomers, where the equilibration occurred faster than the reaction rate. Therefore, although the kinetic selectivity in **2** is complete, it is the thermodynamic preference that can have a greater effect on an asymmetric reaction. In order to evaluate it as an alternative to the previously described phosphine complexes, pure (S_{Ru},*R*)-**2** was obtained using the previously reported BINAM-based resolution procedure [22] and was employed as a catalyst precursor for the aforementioned Diels-Alder reaction (Fig. 4). The reaction proceeded with the usual high *exo* selectivity (95%) and with 23% ee, which is in the same regime as the phosphine complexes (92–98% *exo* and 13–40 % ee) [22,28]. Although this selectivity is modest, it was noted with the phosphine variants that the use of a chiral monodentate phosphine ligand served to increase the enantioselectivity of the reaction, as a matched/mismatched effect was observed [22]. Therefore, the potential remains for a similar improvement with the implementation of chiral NHC ligands.

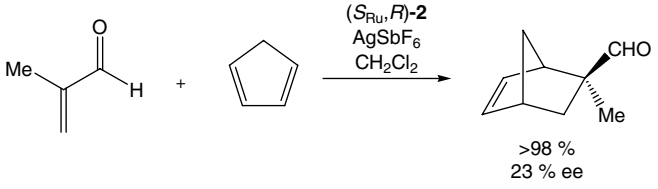

Fig. 4. Asymmetric Diels-Alder Catalysis with 2/$AgSbF_6$.

3. Conclusions

The stereoselective synthesis of arene ruthenium complex **2**, which exhibits both planar chirality and chirality at the metal center, has been described. This protocol, which involves a silver transmetallation where the counterion of the Ag–NHC is BF_4, should be generally applicable for the preparation of transition metal NHC complexes from neutral metal halide precursors. Thus, the use of a Ag–NHC complex with a non-coordinating anion complements the reactivity of the variants with halide counterions. This is the first report, to our knowledge, of an arene ruthenium complex containing both an NHC and a phosphine ligand. Given the precedent for cationic half-sandwich ruthenium complexes in catalysis, these complexes are potentially desirable to many research groups.

The strong *anti* selectivity observed in this synthesis is in accord with what has previously been seen for the phosphine analogues. The X-ray structure of **2** shows planarity of the C–NMe_2 and an interesting pucker of the η^6-ring facilitated by the strong electron-donating power and *trans* influence of the NHC ligand. NMR spectra indicate that these features of the solid-state structure are not rigidly retained in solution. The hindered rotation of the NHC was established from the room temperature NMR spectra, which showed the diastereotopic nature of the two sides of the ligand. Warming to 55 °C resulted in a broadening of certain resonances and from this, a rotational barrier of 17.4 kcal/mol was calculated.

The complex **2** is chiral-at-metal, and the metal-centered chirality is controlled by the planar chirality of the arene-tethered ligand, such that the NHC occupies the *anti* site relative to the NMe_2 group. The non-labile nature of **2** is reflected in the lack of metal epimerization in solution. The application of **2** to the Diels-Alder reaction of methacrolein and cyclopentadiene showed that the product was obtained with high diastereoselectivity (95% *exo*) and modest enantioselectivity (23% ee), this result resembles that for the phosphine analogues. As chiral phosphine ligands have been shown to increase the enantioselectivity for this system, we plan to next investigate the use of chiral NHC ligands, as well as the chirality that would result from a hindered rotation of an unsymmetrical NHC.

4. Experimental

4.1. General

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. CH_2Cl_2 was dried by distillation over CaH in a nitrogen atmosphere, and MeCN was dried on an alumina-based solvent purification system. Ag_2O, $AgBF_4$, $Me_2NC_6H_4C_6H_4PCy_2$ (Strem), methacrolein, dicyclopentadiene, and $Eu(hfc)_3$ (Aldrich) were used as received. The reported procedures were used to prepare 1,3-dibutylimidazolium bromide [32] and **1** [28]. The enantiomerically pure (*R*)-**1** was prepared

using (*R*)-BINAM by conversion to [Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4PCy_2$)(BINAM)]$(SbF_6)_2$, resolution by fractional crystallization, and treatment with HCl [22].

4.2. [anti-Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4PCy_2$)-(1,3-dibutylimidazol-2-ylidene)Cl]BF_4 (**2**)

A flame-dried flask was charged with Ag_2O (250 mg, 1.1 mmol), 1,3-dibutylimidazolium bromide (29 mg, 0.11 mmol), and then CH_2Cl_2 (5 mL). The mixture was stirred for 5 h, filtered through Celite, and dried under vacuum. The resulting brownish residue was added to a flask along with $AgBF_4$ (29 mg, 0.15 mmol) and placed under a nitrogen atmosphere. MeCN (5 mL) was added and the mix was heated to 60 °C for 30 min. The solution was cooled and filtered through Celite. After drying, the filtrate was taken up in CH_2Cl_2 (3 mL) and added to a solution of **1** (56 mg, 0.099 mmol) in CH_2Cl_2 (3 mL) under a nitrogen atmosphere. The solution was stirred for 2 h, filtered, and dried. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2. Yellow crystals were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of the product (51 mg, 65%). Anal. Calc. for $C_{37}H_{56}BClF_4N_3PRu$: C, 55.75; H, 7.08; N, 5.27; Found: C, 55.42; H, 7.04; N, 5.14%. ^{1}H NMR (400 MHz,$CDCl_3$): 7.82 (m, 1H, CH_{arom}), 7.78 (m, 1H, CH_{arom}), 7.57 (t, 1H, $J = 7.6$ Hz, CH_{arom}), 7.49 (t, 1H, $J = 7.6$ Hz, CH_{arom}), 7.16 (d, 1H, $J = 2.0$ Hz, CH_{imid}), 7.08 (d, 1H, $J = 2.0$ Hz, CH_{imid}), 5.93 (dd, 1H, $J = 6.5$, 4.9 Hz, C$H_{\eta6\text{-arene}}$), 5.87 (tm, 1H, $J = 6.5$ Hz, C$H_{\eta6\text{-arene}}$), 4.93 (d, 1H, $J = 6.5$ Hz, C$H_{\eta6\text{-arene}}$), 4.76 (ddd, 1H, $J = 13.2$, 11.0, 5.1 Hz, C$H_{2\,butyl}$), 4.40 (dd, 1H, $J = 4.9$, 1.0 Hz, C$H_{\eta6\text{-arene}}$), 4.26 (ddd, 1H, $J = 13.2$, 10.8, 5.6 Hz, C$H_{2\,butyl}$), 3.10 (br, 1H, C$H_{cyclohexyl}$), 2.95 (ddd, 1H, $J = 13.2$, 12.5, 4.9 Hz, C$H_{2\,butyl}$), 2.78 (ddd, 1H, obscured by another resonance), 2.73 (br, 6H, N(CH_3)$_2$), 2.57 (br, 1H, C$H_{cyclohexyl}$), 2.07–1.03 (m, 28H, C$H_{cyclohexyl}$ and C$H_{2\,butyl}$), 0.96 (t, 3H, $J = 7.4$ Hz, C$H_{3\ butyl}$), 0.68 (t, 3H, $J = 7.0$ Hz, C$H_{3\ butyl}$), 0.61–0.43 (m, 3H, C$H_{cyclohexyl}$ and C$H_{2\,butyl}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): 167.4 (d, $J_{C-P} = 19.3$ Hz. $C_{carbene}$); 147.9 (d, $J_{C-P} = 33.8$ Hz), 145.7 (d, $J_{C-P} = 20.1$ Hz), (C_{arom}); 138.9 ($CN_{\eta6\text{-arene}}$), 132.2, 131.4, 131.3 129.1 (d, $J_{C-P} = 4.8$ Hz), (CH_{arom}); 124.0, 122.5, (CH_{imid}); 94.0 (d, $J_{C-P} = 6.2$ Hz), 93.8, 92.4 (d, $J_{C-P} = 8.2$ Hz), 78.3, 73.8, ($C_{\eta6\text{-arene}}$); 52.0 50.8, ($CH_{2\,butyl}$); 42.9 (br, N(CH_3)$_2$), 40.8 (d, $J_{C-P} = 14.6$ Hz), 40.5 (d, $J_{C-P} = 19.4$ Hz), ($CH_{cyclohexyl}$); 34.0, 33.2, ($CH_{2\,butyl}$); 32.6 (d, $J_{C-P} = 9.1$ Hz), 32.1 (d, $J_{C-P} = 7.7$ Hz), 31.5, 30.3, 28.6–28.2 (several superimposed resonances), 26.3, 26.1, ($CH_{2\ cyclohexyl}$); 20.1, 19.5, ($CH_{2\,butyl}$); 14.1, 13.7, ($CH_{3\ butyl}$). ^{31}P NMR (161.9 MHz, $CDCl_3$): 56.3 (s).

4.3. Diels-Alder catalysis

A flame-dried flask was charged with (S_{Ru},*R*)-**2** and $AgSbF_6$ under a stream of nitrogen. CH_2Cl_2 (3 mL) was added, and the mixture was stirred for 30 min, followed by filtration through Celite to remove the precipitated AgCl. The filtrate was added to a fresh flame-dried flask, and was then subjected to a freeze/pump thaw cycle, and the flask was backfilled with nitrogen. Methacrolein (20 μL, 0.25 mmol) was added at this point, and the flask was allowed to cool to −25 °C before the addition of freshly distilled cyclopentadiene (0.2 mL). The reaction was allowed to proceed at this temperature for 16 h, at which point the volatiles were removed under vacuum. The resulting residue was extracted with Et_2O and dried, giving *exo*-(*S*)-2-methylbicyclo[2.2.1]hept-5-ene-2-carboxaldehyde in 23% ee. The conversion and diastereoselectivity were determined by integration of the aldehyde resonances in the ^{1}H NMR spectrum, and the enantioselectivity was determined with the use of (+)-Eu(hfc)$_3$ as a chiral shift agent in C_6D_6. It was seen that the (*S*)-enantiomer was shifted further downfield.

4.4. Crystal structure determination and refinement

Data were collected on a Nonius KappaCCD (Mo Kα radiation) diffractometer and scaled using HKL2000 [33,34]. The data were not specifically corrected for absorption other than the inherent corrections provided by Scalepack [34]. The structure was solved by direct methods (SIR92) and refined on *F* for all reflections [35,36]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. The structure of the cation has been shown in Fig. 2. Relevant crystal and data parameters are presented in Table 2.

Table 2
Crystallographic data for **2**

Compound **2**	
Color, shape	Yellow, prism
Empirical formula	$C_{37}H_{56}BClF_4N_3PRu$
Formula weight	397.17
Radiation (Å)	Mo Kα (monochr.) 0.71073
T (K)	173
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	
a (Å)	10.1599(3)
b (Å)	12.4738(5)
c (Å)	15.3478(6)
α (°)	101.120(2)
β (°)	95.699(2)
γ (°)	100.540(2)
V (Å^3)	1857.99(12)
Z	2
D_{calc} (g cm^{-3})	1.425
μ (cm^{-1}) (Mo Kα)	5.88
Crystal size (mm)	$0.12 \times 0.12 \times 0.14$
Reflections total, unique, used[a]	15238, 9098; 6640
R_{int}	0.030
Parameters, restraints	433, 0
R[a], R_w[b], Goodness-of-fit	0.034, 0.038, 1.43
Residual density (e Å^{-3})	−0.56 < 1.00

[a] $R = \sum\|\|F_o\| - \|F_c\|\|/\sum|F_o|$, for all $I > 3\sigma(I)$.
[b] $R_w = [\sum[w(|F_o| - |F_c|)^2]/\sum[w(F_o)^2]]^{1/2}$.

Appendix A. Supporting Information

CCDC 618803 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. The metrical parameters are also available in the supporting information. Variable temperature NMR spectra are also shown. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.09.041.

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