

Advances in the Reactivity of Amido-Bridged Binuclear Carbonylruthenium Complexes – Derivative Chemistry of the Cationic Complex $[\text{Ru}_2(\mu\text{-dan})(\mu\text{-H})(\text{CO})_6][\text{BF}_4]$ ($\text{H}_2\text{dan} = 1,8\text{-Diaminonaphthalene}$)

Javier A. Cabeza*, Jorge García-Díez, and Víctor Riera

Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica “Enrique Moles”, Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain

Fax: (internat.) +34-985103446

E-mail: jac@saaron.quimica.uniovi.es

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The reactivity of the cationic amido-bridged binuclear ruthenium carbonyl complex $[\text{Ru}_2(\mu\text{-dan})(\mu\text{-H})(\text{CO})_6]^+$ ($\text{H}_2\text{dan} = 1,8\text{-diaminonaphthalene}$) (**2**) with some anionic and neutral nucleophilic reagents has been investigated. The reaction of **2** with halide anions gives neutral products, $[\text{Ru}_2\text{X}(\mu\text{-dan})(\mu\text{-H})(\text{CO})_5]$ [$\text{X} = \text{Cl}$ (**3**), Br (**4**), I (**5**)], which result from the regiospecific substitution of the halide anion for one of the CO ligands *trans* to the bridging hydride. Compound **3** is more conveniently prepared by treatment of the neutral complex $[\text{Ru}_2(\mu\text{-dan})(\text{CO})_6]$ with gaseous hydrogen chloride. The reaction of **2** with triphenylphosphane affords the disubstituted product of C_{2v} symmetry $[\text{Ru}_2(\mu\text{-dan})(\mu\text{-H})(\text{PPh}_3)_2(\text{CO})_4]^+$ (**7a**), which can be

transformed into the asymmetric isomer **7b** under thermal conditions (70 °C, 10 h) or under acid catalysis ($[\text{HOEt}_2][\text{BF}_4]$, 18 °C, 1 min). Such isomerization reactions can be prevented by adding an excess of triphenylphosphane to the solutions. The complexes **7a** and **7b** can also be prepared by treating the neutral complex $[\text{Ru}_2(\mu\text{-dan})(\text{PPh}_3)_2(\text{CO})_4]$ with $[\text{HOEt}_2][\text{BF}_4]$ in the presence (for **7a**) or in the absence (for **7b**) of triphenylphosphane. In addition, compound **3** reacts with triphenylphosphane at room temperature to give the symmetric cationic complex **7a**, whereas the reaction of complex **5** with triphenylphosphane requires higher temperature and gives the asymmetric isomer **7b**.

Introduction

The interest in the synthesis and reactivity of late-transition-metal amido complexes has grown considerably^[1]. This research activity has been carried out in parallel to investigations on binuclear carbonylruthenium(I) complexes^[2]. In connection with these two research fields, we have previously reported the synthesis of the binuclear amido-bridged carbonylruthenium(I) complex $[\text{Ru}_2(\mu\text{-dan})(\text{CO})_6]$ ($\text{H}_2\text{dan} = 1,8\text{-diaminonaphthalene}$) (**1**)^{[3][4]}. Reactivity studies on compound **1** have shown that it can be protonated at the metal atoms to give the cationic derivative $[\text{Ru}_2(\mu\text{-dan})(\mu\text{-H})(\text{CO})_6]^+$ (**2**) and that it readily undergoes carbonyl substitution reactions with phosphane ligands to give disubstituted derivatives such as $[\text{Ru}_2(\mu\text{-dan})(\text{PPh}_3)_2(\text{CO})_4]$ ^[4]. The basicity and the *cis*-labilizing character of the bridging amido ligand have been suggested as the factors responsible for the observed reactivity. However, compound **1** does not react with hard ligands, such as the halide anions^[5].

As cationic complexes should be more prone than their neutral precursors to undergo reactions with basic reagents^{[6][7]}, and as the protonation of neutral complexes should increase the hard character of the metal atoms, we thought it would be interesting to study the substitution chemistry of the cationic compound **2** and to compare it with that of its neutral precursor **1**. No such a comparative study is known for binuclear complexes, although related

studies with trinuclear carbonylruthenium clusters have been reported^[7].

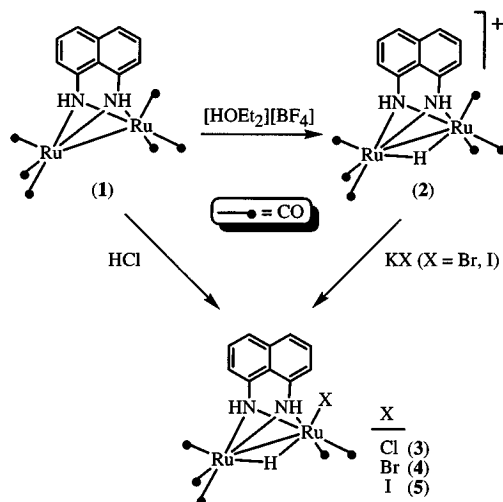
Results and Discussion

Reactions with Halide Anions

Treatment of the ionic compound $[\text{Ru}_2(\mu\text{-dan})(\mu\text{-H})(\text{CO})_6][\text{BF}_4]$ (**2** $[\text{BF}_4]$) with dichloromethane solutions of $[\text{PPN}]\text{X}$ ($\text{X} = \text{Cl}$, Br , I) or $[\text{Et}_4\text{N}]\text{Br}$ led to the instantaneous formation of the neutral derivatives $[\text{Ru}_2\text{X}(\mu\text{-dan})(\mu\text{-H})(\text{CO})_5]$ [$\text{X} = \text{Cl}$ (**3**), Br (**4**), I (**5**)] in quantitative spectroscopic (IR) yields. However, this synthetic method did not lead to analytically pure products because the complexes could not be efficiently separated from the ionic tetrafluoroborate byproducts $\text{Q}[\text{BF}_4]$ ($\text{Q} = \text{PPN}$, Et_4N) by either fractional crystallization (similar solubility in organic solvents) or chromatographic methods (the complexes did not elute on silica and alumina). In addition, treatment of **2** $[\text{BF}_4]$ with an excess of solid KX ($\text{X} = \text{Cl}$, Br , I) in dichloromethane also gave compounds **3–5**, but the reactions were slow. The bromo and iodo complexes **4** and **5** were efficiently prepared in pure form by this method, requiring reaction times of 40 and 20 h, respectively. The reaction of **2** $[\text{BF}_4]$ with KCl was very slow, being incomplete (ca. 70% conversion) after one week. It should be noted that KCl is nearly insoluble in chlorinated solvents, and that **2** $[\text{BF}_4]$ undergoes

deprotonation in basic solvents such as acetone, THF, or water, thus preventing the use of such solvents in the reactions. The most convenient method to prepare the chloro complex **2** in pure form turned out to be the treatment of the neutral hexacarbonyl complex **1** with a dichloromethane solution of HCl.

Scheme 1



The structure proposed for compounds **3–5** in Scheme 1 is based on their analytical and spectroscopic data. Their IR spectra are nearly identical, suggesting a common structure for the three compounds, showing the $\nu(\text{CO})$ absorptions at lower wavenumbers (2115–1985 cm^{-1}) than those of the cationic starting complex **2** (2136–1991 cm^{-1})^[4]. Their ^1H -NMR spectra (Table 1) show one hydride resonance and four resonances for the dan ligand (three aromatic and one NH), indicating the presence of a mirror plane that divides the dan ligand into two identical halves. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of compound **5** (taken as a representative example) shows three carbonyl resonances in a 2:2:1 ratio (relaxation delay 2 s), confirming the presence of five CO ligands. Interestingly, only the smallest carbonyl signal is split into a doublet in the proton-coupled ^{13}C -NMR spectrum, indicating that only one CO ligand is in a *trans* position to the hydride. Thus, these data confirm the structure shown in Scheme 1 and rule out an alternative structure which would have the hydride and halide ligands in terminal and bridging positions, respectively.

It seems that the *acidic* (and not merely the *cationic*) character of complex **2** might be responsible for the observed reactivity. In fact, complex **2** could reversibly protonate the halide anions to give the corresponding hydrogen halides which would then react in a *concerted* way with the conjugated base **1** to give the substituted products **1–3**.

As halide anions are worse π -acceptor ligands than carbon monoxide, the substitution of halide anions for carbonyl ligands in ruthenium complexes has been previously observed only on a few occasions on neutral^{[8][9]} and cationic^{[6b][6c][10]} carbonyl cluster compounds. As mentioned in the Introduction, the neutral compound **1** does not react with halide anions^[5]. Curiously, it has been reported that

Table 1. Comparative ^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR data for compounds **2–7**^[a]

Comp.	$\delta_{\text{H}}(\mu\text{-H})$	$\delta_{\text{H}}(\text{dan})$	$\delta_{\text{P}}(\text{PPh}_3)$
2 ^{[b][c]}	−10.95 (s)	7.82 (d) [7.7], 7.60 (d) [7.7], 7.43 (t) [7.7], 7.56 (s, br.)	
3	−15.30 (s)	7.62 (dd) [7.6, 1.1], 7.25 (t) [7.6], 7.16 (dd) [7.6, 1.1], 5.14 (s, br.)	
4	−14.37 (s)	7.65 (dd) [7.6, 1.1], 7.29 (t) [7.6], 7.35 (dd) [7.6, 1.1], 5.05 (s, br.)	
5	−12.56 (s)	7.60 (dd) [7.6, 1.0], 7.28 (t) [7.6], 7.14 (dd) [7.6, 1.1], 4.85 (s, br.)	
6 ^[b]		6.83 (d) [7.8], 6.39 (t) [7.8], 5.98 (d) [7.8], 4.23 (s, br.)	27.7 (s)
7a	−9.63 (t) {41.4}	6.73 (d) [7.9], 6.54 (d) [7.9], 6.29 (t) [7.9], 5.24 (s, br.)	37.6 (s)
7b	−10.10 (dd) {43.5, 7.4}	7.45 (d) [7.7], 6.85 (t) [7.5], 6.67 (t) [7.7], 5.87 (d) [7.5], 2.26 (s, br.) ^[d]	49.4 (s), 38.9 (s)

^[a] Spectra recorded in CDCl_3 ; multiplicities are given in parentheses; coupling constants (Hz) are given in square brackets [$J_{\text{H-H}}$] or braces [$J_{\text{H-P}}$]. — ^[b] Data taken from ref.^[4]. — ^[c] Spectrum recorded in $(\text{CD}_3)_2\text{CO}$ containing 10% $[\text{HOEt}_2][\text{BF}_4]$. — ^[d] Other resonances of the dan ligand are obscured by those of the PPh_3 ligand.

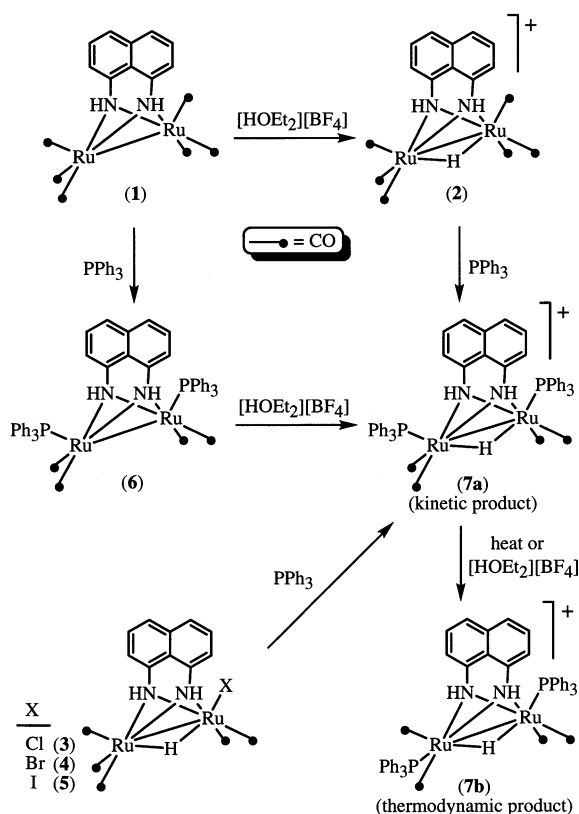
the anionic binuclear osmium(I) complexes $[\text{PPN}][\text{Os}_2\text{X}(\mu\text{-O}_2\text{CMe})_2(\text{CO})_5]$ ($\text{X} = \text{Cl}, \text{I}$) can be prepared by treatment of the solvated complex $[\text{Os}_2(\mu\text{-O}_2\text{CMe})_2(\text{CO})_5(\text{thf})]$ with $[\text{PPN}]\text{X}$ ^[11]. Unfortunately, all attempts to prepare any solvated derivative of complex **1** were unsuccessful.

Reactions with Triphenylphosphane

Complex **2** reacted instantaneously with triphenylphosphane at room temperature to give the disubstituted derivative $[\text{Ru}_2(\mu\text{-dan})(\mu\text{-H})(\text{PPh}_3)_2(\text{CO})_4]^+$ (**7a**), regardless of the ratio of the reactants. The use of a phosphane/complex ratio smaller than two resulted in a mixture of **7a** and unreacted **2**. The symmetric (C_{2v}) structure shown for the cation **7a** in Scheme 2 is based on spectroscopic data. The $^{31}\text{P}\{^1\text{H}\}$ - and ^1H -NMR spectra (Table 1) are consistent with the existence of two mirror planes, since they only show one singlet in the $^{31}\text{P}\{^1\text{H}\}$ spectrum and five resonances in the ^1H spectrum (four for the dan ligand and one for the hydride). In particular, the hydride resonance is a triplet with a large $J(\text{H-P})$ coupling constant (41.4 Hz). It is generally accepted that large (> 20 Hz) $^2J(\text{H-P})$ coupling constants are indicative of a *trans* arrangement of hydride and phosphane ligands on a metal carbonyl complex^[7], although some exceptions to this rule have been reported for pentacoordinated iron complexes^[12].

In an attempt to make **7a** $[\text{BF}_4]$ by an alternative route, we treated a dichloromethane solution of the symmetric (C_{2v}) neutral disubstituted compound $[\text{Ru}_2(\mu\text{-dan})(\text{PPh}_3)_2(\text{CO})_4]$ (**6**) with an excess of $[\text{HOEt}_2][\text{BF}_4]$ in diethyl ether. The reaction was instantaneous but, to our surprise, the product was not **7a** but the asymmetric isomer **7b** (Scheme 2), as inferred from its $^{31}\text{P}\{^1\text{H}\}$ spectrum, which consists of two singlet resonances, and from its ^1H spectrum, which shows

Scheme 2



the hydride resonance as a doublet of doublets with $J(\text{H-P})$ coupling constants (43.5 and 7.4 Hz) in agreement with a structural assignment in which the hydride is *trans* to a phosphorus atom and *cis* to the other^[7].

The reactions of the halide derivatives **3** and **5** with triphenylphosphane were also studied. The chloro complex **3** reacted slowly (6 h) with two equivalents triphenylphosphane in 1,2-dichloroethane at room temperature to give the symmetric cationic derivative **7a**. No monosubstituted derivatives were detected when the reaction was monitored by IR or $^{31}\text{P}\{^1\text{H}\}$ NMR. Curiously, no reaction was observed with the iodo derivative **5** under the same conditions, but it gave the asymmetric cationic derivative **7b** within 30 min when the reaction was carried out at reflux.

The above results prompted us to try to establish whether the transformations of **7a** into **7b** or of **7b** into **7a** were possible. We found that (a) complex **7a** can be quantitatively transformed into **7b** under thermal conditions (1,2-dichloroethane, reflux temperature) and that the rate of the cation isomerization depends on the accompanying anion, being faster for chloride (30 min) than for tetrafluoroborate (10 h), (b) the isomerization reaction is catalysed by acids, since the addition of $[\text{HOEt}_2][\text{BF}_4]$ to a dichloromethane solution of **7a** at room temperature resulted in its instantaneous transformation into **7b**, (c) this isomerization process is inhibited by the presence of free triphenylphosphane, regardless of the presence of acid in the solution, and (d) by no means could the transformation of **7b** into **7a** be achieved. Therefore, it is clear that **7a** is the kinetic isomer

and that **7b** is the thermodynamic isomer, and that the isomerization takes place through a dissociative mechanism which requires the decoordination of triphenylphosphane in the activation step.

To our knowledge, no previous isomerization reactions of phosphane-substituted ligand-bridged binuclear ruthenium complexes have been described, but a few examples of such reactions have been reported for trinuclear clusters^[7].

Further work on the reactivity of binuclear cationic carbonylruthenium complexes, extending the reactions to other P-donor ligands, such as phosphites, diphosphanes, etc., is in progress.

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Experimental Section

General: IR: Perkin-Elmer FT 1720-X. – NMR: Bruker AC-200 and AC-300, 20°C, internal TMS (for ^1H and ^{13}C) or external 85% H_3PO_4 (for ^{31}P) as standards. – Microanalyses: Perkin Elmer 2400. – Solvents were dried with sodium diphenyl ketyl (diethyl ether, hydrocarbons) or CaH_2 (dichloromethane, 1,2-dichloroethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen with Schlenk vacuum-line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). Compounds **1**, **2**, and **6** were prepared as described previously^[4]. A saturated solution of HCl in dichloromethane was prepared by bubbling gaseous HCl (formed by addition of 98% sulfuric acid to solid NaCl) through the solvent. All the other reagents were purchased from Aldrich and were used as received.

$[\text{Ru}_2\text{Cl}(\mu\text{-dan})(\mu\text{-H})(\text{CO})_5]$ (**3**): A saturated solution of HCl in dichloromethane (2 ml) was added to a solution of compound **1** (100 mg, 0.190 mmol) in the same solvent (10 ml). The original pale yellow colour slightly darkened and the IR spectrum of the resulting solution revealed the complete transformation of **1** into a new compound. The solvent was removed under reduced pressure and the residue was washed with hexane (2×10 ml) and dried to give complex **3** as a yellow solid (83 mg, 82%). – $\text{C}_{15}\text{H}_9\text{ClN}_2\text{O}_5\text{Ru}_2$ (534.86); calcd. C 33.68, H 1.70, N 5.24; found C 33.21, H 1.46, N, 4.91. – IR (CH_2Cl_2): $\tilde{\nu} = 2115\text{ cm}^{-1}$ (m), 2053 (s), 1985 (m).

$[\text{Ru}_2\text{Br}(\mu\text{-dan})(\mu\text{-H})(\text{CO})_5]$ (**4**): Solid KBr (96 mg, 0.807 mmol) was added to a solution of **2** $[\text{BF}_4]$ (50 mg, 0.081 mmol) in dichloromethane (10 ml). The resulting suspension was stirred for 40 h, when the IR spectrum of the solution revealed the absence of the starting material. The suspension was filtered through a Celite filter and the resulting yellow solution was concentrated to dryness. The solid residue was washed with hexane (2×5 ml) and dried to give complex **4** as a yellow solid (35 mg, 75%). – $\text{C}_{15}\text{H}_9\text{BrN}_2\text{O}_5\text{Ru}_2$ (579.31); calcd. C 31.10, H 1.57, N 4.84; found C 30.91, H 1.66, N 4.65. – IR (CH_2Cl_2): $\tilde{\nu} = 2115\text{ cm}^{-1}$ (m), 2052 (s), 1987 (m).

$[\text{Ru}_2\text{I}(\mu\text{-dan})(\mu\text{-H})(\text{CO})_5]$ (**5**): Solid KI (132 mg, 0.795 mmol) was added to a solution of **2** $[\text{BF}_4]$ (50 mg, 0.081 mmol) in dichloromethane (10 ml). The resulting suspension was stirred for 20 h, when the IR spectrum of the solution revealed the absence of the starting material. The suspension was filtered through a Celite filter and the resulting solution was concentrated to dryness. The solid residue was washed with hexane (2×5 ml) and dried to give complex **5** as a yellow-orange solid (34 mg, 67%). – $\text{C}_{15}\text{H}_9\text{IN}_2\text{O}_5\text{Ru}_2$

(626.31): calcd. C 28.77, H 1.45, N 4.47; found C 28.51, H 1.58, N 4.09. – IR (CH₂Cl₂): $\tilde{\nu}$ = 2114 cm⁻¹ (m), 2051 (s), 1986 (m). – ¹³C{¹H} NMR (CD₂Cl₂): δ = 196.9 (2 CO), 190.2 (2 CO), 181.9 (1 CO), 148.7 (2 C), 135.4 (1 C), 126.1 (2 C), 125.3 (1 C), 124.5 (2 C), 114.7 (2 C) (all singlets); the resonances at δ = 181.9, 126.1, 124.5, and 114.7 are split into doublets in the proton-coupled spectrum.

[Ru₂(μ -*dan*)(μ -H)(PPh₃)₂(CO)₄][BF₄] (**7a**[BF₄], symmetric isomer): Solid **2**[BF₄] (25 mg, 0.041 mmol) was added to a stirred solution of PPh₃ (22 mg, 0.084 mmol) in dichloromethane (10 ml). The reaction was instantaneous (IR). No changes were observed in the IR spectrum of this solution after 20 h. The solvent was removed under reduced pressure and the residue was washed with hexane (2 $\times$ 5 ml) and dried to give **7a**[BF₄] as a yellow solid (36 mg, 80%). – C₅₀H₃₉BF₄N₂O₄P₂Ru₂ (1082.79): calcd. C 55.46, H 3.63, N 2.59; found C 54.92, H 3.94, N 2.30. – IR (CH₂Cl₂): $\tilde{\nu}$ = 2063 cm⁻¹ (s), 2047 (m), 1998 (s).

[Ru₂(μ -*dan*)(μ -H)(PPh₃)₂(CO)₄][BF₄] (**7b**[BF₄], asymmetric isomer): An excess of [HOEt₂][BF₄] (0.2 ml, 60% solution in diethyl ether) was added to a solution of complex **6** (100 mg, 0.100 mmol) in dichloromethane (10 ml). The reaction was instantaneous (IR). The solvent was removed under reduced pressure and the oily residue was washed with diethyl ether (3 $\times$ 5 ml) and dried to give **7b**[BF₄] as a yellow solid (87 mg, 80%). – C₅₀H₃₉BF₄N₂O₄P₂Ru₂ (1082.79): calcd. C 55.46, H 3.63, N 2.59; found C 55.42, H 3.83, N 2.39. – IR (CH₂Cl₂): $\tilde{\nu}$ = 2063 cm⁻¹ (m), 2051 (s), 2000 (s). – ¹³C{¹H} NMR (CDCl₃): δ = 196.5 (d, *J* = 11.1 Hz, 1 CO), 196.4 (d, *J* = 12.6 Hz, 1 CO), 194.7 (d, *J* = 12.9 Hz, 1 CO), 190.4 (t, *J* = 10.9 Hz, 1 CO), 150.3 (1 C), 147.4 (1 C), 135–112 (complex mixture of signals).

Protonation of Complex 6 in the Presence of Triphenylphosphane: An excess of [HOEt₂][BF₄] (0.2 ml, 60% solution in diethyl ether) was added to a solution of PPh₃ (105 mg, 0.400 mmol) and complex **6** (100 mg, 0.100 mmol) in dichloromethane (10 ml). After 3 min, the IR spectrum of the resulting solution showed only the presence of the symmetric complex **7a**, remaining unchanged after 12 h. The solvent was removed under reduced pressure and the residue was washed with diethyl ether (3 $\times$ 5 ml) and dried to give pure **7a**[BF₄] (IR, ³¹P NMR) (75 mg, 69%).

Reaction of Complex 3 with Triphenylphosphane: A solution of complex **3** (100 mg, 0.187 mmol) and triphenylphosphane (98 mg, 0.375 mmol) in 1,2-dichloroethane (10 ml) was stirred at room temperature for 6 h, when the IR spectrum of the solution showed the complete transformation of **3** into the symmetric cationic derivative **7a**.

Reaction of Complex 5 with Triphenylphosphane: A solution of complex **5** (35 mg, 0.056 mmol) and triphenylphosphane (30 mg, 0.113 mmol) in 1,2-dichloroethane (10 ml) was stirred at room tem-

perature for 1 h, but no reaction was observed (IR). The solution was then heated to reflux temperature. After 30 min, the IR spectrum showed the complete transformation of **5** into the asymmetric cationic derivative **7b**.

Thermal Isomerization of 7a to 7b: A solution of **7a**[BF₄] (50 mg, 0.046 mmol) in 1,2-dichloroethane (20 ml) was stirred at reflux temperature. The reaction was monitored by IR spectroscopy, which showed the complete transformation of **7a** into **7b** after 10 h. When the chloride salt **7a**[Cl] was used as starting material, under analogous conditions, the transformation of **7a** into **7b** took only 30 min.

Acid-Catalysed Isomerization of 7a to 7b: [HOEt₂][BF₄] (0.2 ml, 60% solution in diethyl ether) was added to a solution of **7a**[BF₄] (50 mg, 0.046 mmol) in dichloromethane (20 ml). The IR spectrum of the resulting solution showed the complete transformation of **7a** into **7b**.

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