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PGSE diffusion NMR studies on mononuclear and dinuclear cationic platinum salts of (S)-MeO-Biphep and (R)-p-tolyl-BINAP

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Abstract

PGSE diffusion NMR studies on a series of mononuclear and dinuclear cationic platinum salts derived from (*S*)-MeO-Biphep and (*R*)-*p*-tolyl-BINAP are reported. The data show that (a) one can readily distinguish between mononuclear and dinuclear cations (b) the amount of ion pairing can be estimated qualitatively and (c) the charge delocalization rather than the amount of formal charge per metal cation is important for the position of the anion. The solid-state structure of the chloro-bridged salt, $[Pt(\mu-Cl){(S)-MeO-Biphep}]_{CF_3SO_3)_2}$, is reported.

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1. Introduction

There is a growing interest in measuring diffusion constants and several methodologies are currently in use. These include attenuated total reflection infrared spectroscopy [1], capacity intermittent titration techniques [2], long capillary methods [3], and pulsed field gradient spin echo (PGSE) NMR spectroscopy.

In the PGSE Stejskal–Tanner experiment, Fig. 1, transverse magnetization is generated by the initial $\pi/2$ pulse. This magnetization dephases due to chemical shift, heteroand homo-nuclear coupling evolution, and T_2 relaxation. After application of the second π pulse, the magnetization refocuses, generating an echo. The first of two pulsed gradients results in strong dephasing of the magnetization (signal loss). Because the strength of the gradient varies linearly along, e.g., the z-axis, only spins contained within a narrow slice of the sample acquire the same phase angle. The second gradient pulse reverses the respective phases and the echo forms. Spins, which diffuse out of their slice into neighboring areas, via Brownian motion, will not be refocused by the second gradient and this leads to an *attenuation* of the echo amplitude. As smaller molecules move faster, they translate during the time interval Δ into slices further apart from their origin, thus giving rise to smaller spin echo intensities.

The amplitude of the echo can be expressed by:

$$\ln\left(\frac{I}{I_0}\right) = -(\gamma\delta)^2 G^2 \left(\Delta - \frac{\delta}{3}\right) D \tag{1}$$

where G is the gradient strength, Δ is the delay between the midpoints of the gradients, D is the diffusion coefficient, and δ is the gradient length. The diffusion coefficient, D, is obtained by plotting $\ln(I/I_0)$ (I/I_0 = observed spin echo intensity/intensity without gradients) versus either Δ , δ^2 , ($\Delta - \delta/3$) or G^2 .

NMR diffusion methods are now routinely in use and the basic experiment has been reviewed [4–11]. In more recent reviews Cohen and co-workers [10], apply diffusion NMR spectroscopy in supra-molecular and combinatorial chemistry, whereas Berger and co-workers [11], center on

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Fig. 1. Pulse sequences for the PGSE measurements.

intermolecular interactions as investigated by both NOE and diffusion studies. An extensive compilation of diffusion constants from PGSE measurements has just appeared [12].

The experimental values for diffusion constants are usually given in units of 10^{-10} m² s⁻¹ and often these values are not familiar to chemists. Consequently, the hydrodynamic radius, $r_{\rm H}$, of the species is also normally calculated, using the Stokes–Einstein relation:

$$D = \frac{kT}{6\pi\eta r_{\rm H}}\tag{2}$$

where k is the Boltzmann constant, T is the absolute temperature, η the viscosity and $r_{\rm H}$ the hydrodynamic radius.

There is a continuing discussion in the literature concerned with "anion effects" [13-24] in coordination chemistry and catalysis. The observed effects of the anion may involve complexation, steric blocking or ion pairing, to name just a few possibilities. Occasionally anion hydrolysis will further complicate matters [25,26]. Unfortunately, it is not always simple to "separate out" the ion pairing contribution. Relative to other physical methods, an analysis of the *D* values via PGSE NMR studies is both rapid and instructive. If the diffusion characteristics of the anion and cation can be measured separately, then inspection of the regression lines for the cation and anion provides a direct estimate of the ion pairing.

Given the general interest in group 10 cationic complexes, we have prepared



several dicationic platinum salts of (S)-MeO-Biphep and (R)-p-tolyl-BINAP, and report here details of our diffusion measurements on these species.

2. Results and discussion

The dicationic platinum complexes $[Pt(u-Cl){(S)-MeO-}]$ Biphep} $b(X)_2$ and $Pt(CH_3CN)_2\{(S)-MeO-Biphep\}(X)_2$, $X = CF_3SO_3^-$ and BF_4^- , plus several BINAP analogs, were prepared as indicated in Scheme 1. The neutral PtCl₂ (diphosphine), which served as a starting material for the syntheses of the dications, was also measured and served as a model species. During the course of the preparation of the salt, $[Pt(CH_3CN)_2\{(S)-MeO-Biphep\}](BF_4)_2$, a low frequency ¹H resonance, $\delta = -1.38$, associated with a minor component, was observed. As this chemical shift was known to be typical for hydroxo-bridged complexes the presumed salt, $[Pt(\mu-OH)](S)$ -MeO-Bip-[27]. hep}] $_{2}(BF_{4})_{2}$, was prepared independently (see Section 4), as indicated in Scheme 1, and shown, indeed, to be the minor species.

Given the increasing use of MeO-Biphep complexes [28–31], the 1 H and 13 C characteristics of the salts were



75 % Yield, for (S)-MeO-Biphep

Scheme 1.



- obtained by 2D NMR methods, Fig. 2 shows the ¹H spectrum for $[Pt(CH_3CN)_2\{(S)-MeO-Biphep\}](CF_3SO_3)_2$, and a number of points are worthy of note:
- 1. There is a very broad resonance, δ ca. 7.75, due to the dynamics associated with restricted rotation in such atropisomeric complexes [32].



Fig. 3. ¹H, ¹H COSY spectrum of [Pt(CH₃CN)₂{(S)-MeO-Biphep}](CF₃SO₃)₂ in the aromatic region, identifying H3–H5.

- 2. The three low frequency proton signals, between δ ca. 6.6 and δ ca. 7.2, are associated with the biaryl backbone moiety and not with the P-phenyl rings (see the ¹H, ¹H correlation in Fig. 3 and the ¹³C, ¹H long-range correlation in Fig. 4) and
- 3. The remaining well resolved proton resonance, at δ ca. 7.48, arises from the *meta* protons of the P-phenyl rings (see Fig. 5).

A selection of ¹³C assignments is given in the experimental section.

2.1. Diffusion results

Table 1 shows the *D* values and the hydrodynamic radii, $r_{\rm H}$ (Å), for the Pt-salts, measured as 2 mM solutions in CD₂Cl₂. Two points are clear:

 The difference in size between the mono-and dinuclear species is reflected in their r_H values, thus supporting the view that PGSE measurements are useful structure probes. As an example, the cation r_H values for [Pt(CH₃CN)₂{(S)-MeO-Biphep}](CF₃SO₃)₂, 6.6 Å, and $[Pt(\mu-Cl){(S)-MeO-Biphep}]_2(CF_3SO_3)_2$, 8.1 Å, are clearly quite different. Similarly, the cation $r_{\rm H}$ values for $[Pt(CH_3CN)_2\{(R)-p-tol-BINAP\}](CF_3SO_3)_2$, 7.1 Å, and $[Pt(\mu-Cl){(R)-p-tol-BINAP}]_{2}(CF_{3}SO_{3})_{2}$ 8.6 Å, also support this idea while showing that the (R)-p-tol-BINAP salts are, as expected, larger than $\{(S)$ -MeO-Biphep analogs. The $r_{\rm H}$ values for the two neutral dichloro-complexes, $PtCl_2\{(S)-MeO-Biphep\}$, 5.9 Å and $PtCl_{2}(R)$ -p-tol-BINAP], 6.5 Å, are in agreement with the difference in size between these two chelating diphosphine compounds. Further, we note (a) that the $r_{\rm H}$ value for the cation of $[Pt(\mu-OH)](S)-MeO-Bip$ hep}]₂(BF₄)₂, 7.8 Å, is consistent with a dinuclear species and (b) that the r_{X-ray} from the solid-state structure of $[Pt(\mu-Cl){(S)-MeO-Biphep}]_2(CF_3SO_3)_2$, 7.8 Å, is in good agreement with the hydrodynamic radius calculated for the same cation in CD₂Cl₂. Correlations between $r_{H(NMR)}$ and r_{X-ray} are known [12] and usually reasonable.

2. Using the $r_{\rm H}$ values for the *anion* as an indication of the ion pairing, one notes that there seems to be more ion pairing of the CF₃SO₃⁻ anion in the dinuclear species [Pt(μ -Cl){(*S*)-MeO-Biphep}]₂(CF₃SO₃)₂, $r_{\rm H}$ (anion) =



Fig. 4. ${}^{13}C, {}^{1}H$ multiple bond correlation spectrum for [Pt(CH₃CN)₂{(*S*)-MeO-Biphep}](CF₃SO₃)₂ which assigns the MeO-Biphep backbone proton, H4, at 7.17 ppm, via a ${}^{3}J({}^{13}C, {}^{1}H)$ interaction with the *ipso-C*-OMe resonance at 157.8 ppm.



Fig. 5. HOESY spectrum for $[Pt(\mu-Cl){(S)-MeO-Biphep}]_2(CF_3SO_3)_2$; ca. 10 mM in CD₂Cl₂. Note the absence of a contact to H5 and the barely detectable cross-peak from the methoxy-group.

5.5 Å, than for the $CF_3SO_3^-$ in the *bis*-nitrile, [Pt-(CH₃CN)₂{(*S*)-MeO-Biphep}](CF₃SO₃)₂, r_H (anion) = 4.8 Å. In the absence of significant ion pairing, e.g., a salt containing the CF₃SO₃ anion dissolved in methanol solution, an r_H value for the anion of ca. 3 Å is expected [7–9,12]. Consequently, in both the Pt dications, there is a substantial amount of ion pairing. For the (*S*)-MeO-Biphep salts, the BF₄⁻ anions show the same trend, although the amount of ion pairing seems to be somewhat smaller for this anion, relative to the triflate salts.¹

2.2. ¹H, ¹⁹F Overhauser results

As it was not obious why the dinuclear salts, e.g., $[Pt(\mu-Cl){(S)-MeO-Biphep}]_2(CF_3SO_3)_2$, with the two positive charges spread across two metals, should show more ion pairing than for the mononuclear dicationic *bis*-nitrile, $[Pt(CH_3CN)_2{(S)-MeO-Biphep}](CF_3SO_3)_2$, several ¹H, ¹⁹F Overhauser (HOESY) spectra were measured. The HOESY spectrum (see Fig. 5) for the dinuclear MeO-Biphep salt shows strong cross peaks which arise from the protons of the P-phenyls (which are expected [6–9,12]) but also



fragment of the MeO-Biphep in

 $[Pt(\mu-Cl){(S)-MeO-Biphep}]_2(CF_3SO_3)_2$,

two fairly strong cross-peaks from two of the three MeO-Biphep biaryl protons, H-3 and H-4, but nothing to H-5 and only a very weak signal from the methoxy-group. This suggests that the anion is localized close to the P-phenyl groups, i.e., close to the platinum atom and the partially positively charged P-atoms. In the analogous HOESY spectrum for the *bis*-nitrile (not shown), *there are no cross-peaks to either of the backbone protons H-3 or H-4*.



However, there are now new, strong, cross-peaks to the methyl groups of the complexed acetonitrile ligands, plus strong cross peaks to the P-phenyl protons, as noted previously. Obviously the positive charge on the cation is spread over the two N-atoms as well as on the two P-atoms (and, of course, the Pt). This dispersion of the positive charge over a larger number of atoms rationalizes the observation that the ion pairing to the $CF_3SO_3^-$ is not quite so pronounced in this mononuclear dicationic complex. Macchioni and co-workers, [33–39] in an extensive series of papers involving ¹H, ¹⁹F HOESY measurements, have shown that

¹ In methanol solution a typical $r_{\rm H}$ value for the BF₄⁻ anion would be ca. 2.5 Å. For the triflate, one cannot readily distinguish between ion pairing, alone, and partial complexation together with partial ion pairing.

with the arrows showing the HOESY contacts

Table 1

Dication		(S)-MeO-Biphep		(R)-p-tol-BINAP	
		D^{a}	r _H	$\overline{D^{\mathrm{a}}}$	$r_{ m H}$
Pt(Cl) ₂ (P-P)		8.92	5.9	8.21	6.5
$\left[Pt(\mu\text{-}Cl)(P\!\!-\!\!P) \right]_2{}^{2+}$	cation CF ₃ SO ₃ ⁻	6.53 9.54	8.1 5.5	6.17 9.40	8.6 5.6
$Pt(CH_3CN)_2(P-P)^{2+}$	cation CF ₃ SO ₃ ⁻	8.07 11.13	6.6 4.8	7.5 9.84	7.1 5.4
$\left[Pt(\mu\text{-}Cl)(P\text{-}P) \right]_2{}^{2+}$	cation BF_4^-	6.64 10.51	8.0 5.0		
$Pt(CH_3CN)_2(P-P)^{2+}$	cation	8.05 6.82 ^b	6.6 7.8		
	$\mathrm{BF_4}^-$ $\mathrm{BF_4}^{-\mathrm{d}}$	13.67 13.53	3.9 3.9		
$\left[Pt(\mu\text{-}OH)(P\text{-}P)\right]_2{}^{2+}$	cation BF₄ [−]	6.82 not measurable, to	7.8 o broad at RT		

Values for the diffusion coefficient, $D (\times 10^{-1})$	10 m ² s ⁻¹) and the hydrodynamic radii, $r_{\rm l}$	$r_{\rm H}$ (Å), in 2 mM CD ₂ Cl ₂ solutions ^a for the Pt-salts
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^a CH₂Cl₂ η (299 K, kg s⁻¹ m⁻¹): 0.414. The values for ¹⁹F were corrected to the gyromagnetic ratio relative to ¹H. The cations were measured via ¹H, the anions via ¹⁹F NMR.

^b Impurity.



Fig. 6. A view of the dinuclear Pt chloro-bridged MeO-Biphep dication. Selected bond distances (Å) and angles (°): Pt(1)–Pt(1) 3.5805(7), Pt(1)–P(2) 2.236(1), Pt(1)–P(1) 2.244(1), Pt(1)–Cl(1)' 2.373(1), Pt(1)–Cl(1) 2.389(1); P(2)–Pt(1)–P(1) 93.26(5), P(2)–Pt(1)–Cl(1)' 92.39(5), P(1)–Pt(1)–Cl(1)' 172.20(5), P(2)–Pt(1)–Cl(1) 172.26(5), P(1)–Pt(1)–Cl(1) 92.45(4), Cl(1)'–Pt(1)–Cl(1) 82.46(5), Pt(1)'–Cl(1)–Pt(1) 97.47(4). Primed atoms are obtained from those of the asymmetric unit by the symmetry operation: (1 - x) + 1; -y; z. Ellipsoids drawn at 50% probability.

unsaturated nitrogen donor ligands in cationic complexes are often associated with a substantial amount of positive charge and, therefore, that the anions are attracted to these ligands.

2.3. Solid-state structure of $[Pt(\mu-Cl)\{(S)-MeO-Biphep\}]_2(CF_3SO_3)_2$

The structure of this dicationic dinuclear Pt-complex was determined via X-ray diffraction methods. There are two independent half molecules in the asymmetric unit located across a binary axis that generates the two "Pt(μ -Cl)₂Pt" dimers in the crystallographic unit cell. The geometries of the two cations do not differ significantly and, therefore, only a view of one of the two dications, together with selected bond parameters, is given in Fig. 6. The immediate coordination sphere around each Pt atom consists of the two P-atoms from a coordinated MeO-Biphep chelate and the two bridging chloride ligands. The Ptligand–atom bond lengths and the coordination bond angles are rather standard and a selection of these is given in the caption to Fig. 6. There is no bending of the Pt(Cl)₂Pt four-membered ring (i.e., no butterfly type structure), due to the crystallographic symmetry, and the two Pt-atoms are sufficiently far apart, Pt(1)-Pt(1)' =3.5805(7) Å, such that a metal-metal bonding interaction is extremely unlikely. The two P-phenyl groups on any one P-atom occupy pseudo-equatorial and pseudo-axial positions with respect to the plane defined by the two P-atoms, the metal and the two bridging halogens.

3. Conclusions

Once again the PGSE diffusion methodology shows itself to be useful in connection with recognizing mono-versus dinuclear complexes in solution. The amount of ion pairing can be estimated qualitatively, and, when taken together with ¹H, ¹⁹F Overhauser data, one obtains a view as to where the anion resides and, thus, why one type of salt might reveal more ion pairing than a related species.

4. Experimental

4.1. General Comments

All air sensitive manipulations were carried out under a nitrogen atmosphere. All solvents were dried over appropriate drying agents, distilled under nitrogen. Deuterated solvents were dried by distillation over molecular sieves, and stored under nitrogen. The ligands (R)-p-tolyl-BINAP (Strem) and the silver salts (Aldrich) were purchased from commercial sources and used as received. The (S)-MeO-Biphep was a gift from F. Hoffmann La-Roche, Basel, Switzerland. The *bis*-tetrahydrothiophene (THT) complex PtCl₂(THT)₂ was synthesized in our laboratory according to literature methods [40].

NMR spectra were recorded with Bruker DPX-300, 400 and 500 and 700 MHz spectrometers at room temperature unless otherwise noted. Elemental analysis and mass spectra were performed at ETH Zürich.

4.2. General procedure (NMR)

 1 H, 31 P, 13 C and 19 F NMR spectra were recorded on Bruker Avance 300, 400, 500 NMR spectrometers. Deuterated solvents were dried by distillation over molecular sieves, and stored under N₂.

4.3. Diffusion

All the PGSE NMR measurements were performed on a Bruker Avance spectrometer, 400 MHz, equipped with a microprocessor-controlled gradient unit and a multinuclear inverse probe with an actively shielded Z-gradient coil. The gradient shape is rectangular and its length was 1.75 ms. The gradient strength was increased by steps of 4% during the course of the experiment. The time between midpoints of the gradients was 167.75 ms for all experiments. The

experiments were carried out at a set temperature of 299 K within the NMR probe.

As indicated in Table 1, diffusion values were measured on 2 mM dichloromethane solutions. Cation diffusion rates were measured using the ¹H signal from either the aromatic, MeO, or CH₃CN protons depending on the ¹H spectrum considered. Anion diffusion data was obtained from the ¹⁹F NMR spectrum of the anion. The error in the *D* values is thought to be ± 0.06 .

4.4. HOESY

 $^{19}\text{F}^{-1}\text{H}$ HOESY spectra were measured at concentrations of 10 mM, in dichloromethane solutions, at 299 K with a 0.8 s mixing time.

4.5. $PtCl_2((S)-MeO-Biphep)$

 $PtCl_2(SC_4H_8)$ (500 mg, 442.3 g mol⁻¹, 1.13×10^{-3} mol) and (S)-Meo-Biphep (659 mg, 582.6 g mol⁻¹, 1.13×10^{-3} mol) were placed in a Schlenk vessel. CH₂Cl₂ (15 mL) was added under nitrogen and the resulting yellow solution was stirred during approximately 14 h. The CH₂Cl₂ was removed i.v. and the resulting pale yellow solid was washed several times with hexane in order to remove excess (S)-Meo-Biphep and free SC₄H₈. After drying one obtains 680 mg, 72%, of product. NMR: ¹H (CH₂Cl₂, 299 K, 300 MHz) 7.84 (b, ortho-phenyl ring a), 7.68 (m, ortho-phenyl ring b), 7.48 (m, meta-phenyl b), 7.45 (m, para-phenyl rings a and b), 7.30 (meta-phenyl ring a), 6.96 (dd, H4), 6.72 (H3), 6.46 (d, H5), 3.52 (s, OMe); ${}^{31}P$ (CH₂Cl₂, 299 K, 121 MHz) 8.13 (J_{PPt} 3647 Hz); ${}^{13}C$ (CH₂Cl₂, 299 K, 75 MHz) 55.0 (s, OMe), 112.7 (s, C5), 124.7 (C3) 127.2 (meta-phenyl ring), 127.8 (tb, meta-phenyl ring), 129.2 (C4), 130.7 (s, *para*-phenyl ring), 131.4 (s, *para*-phenyl ring), 135.2 (tb, ortho-phenyl ring), 157.5 (tb, quaternary MeO-C); EA: Anal. Calc for C₃₈H₃₂O₂Cl₂P₂- Pt(H₂O): C, 52.68; H, 3.92. Found: C, 52.69; H, 3.89%.

4.6. $[Pt(\mu-Cl)((S)-MeO-Biphep)]_2[CF_3SO_3]_2$

Under an N₂ atmosphere; $PtCl_2((S)-MeO-Biphep)$ (60 mg, 7.07×10^{-5} mol) was dissolved in 5 mL of CH₂Cl₂ in a Schlenk tube. AgCF₃SO₃ (18.16 mg, 7.07×10^{-5} mol) was suspended in yet another 5 mL of CH₂Cl₂. and after stirring for 15 min, the AgCF₃SO₃ suspension was transferred into the PtCl₂((S)-MeO-Biphep) solution. After stirring for 1 h, the white-grey solid, suspended in the pale yellow solution is filtered over Celite via canula. The solvent is reduced i.v. and the resulting solid is dried: Yield: 56 mg, 82%. NMR: ¹H (CH₂Cl₂, 299 K, 300 MHz) 7.69 (*ortho*-phenyl ring a) 7.63 (*meta*-phenyl ring a), 7.52 (*para*-phenyl ring b), 7.13 (H4). 7.05 (H3), 6.55 (d, H5), 3.45 (s, OMe); ³¹P (CH₂Cl₂, 299 K, 75 MHz) 55.2 (s, OMe), 114.4 (s, C5), 124.7 (C4), 129.0 (*meta*-phenyl ring a), 130.3 (C3), 132.1 (*para*-phenyl ring b), 132.9 (*para*-phenyl ring a), 135.0 (*ortho*-phenyl ring), 157.8 (quaternary MeO-*C*); ¹⁹F (CH₂Cl₂, 299 K, 282.3 MHz) –79.2 (s). MS: 812.9 Pt(Cl)((*S*)-MeO-Biphep) 775.9 Pt((*S*)-MeO-Biphep). EA: Calc.: C, 47.48; H, 3.35. Found: C, 47.54; H, 3.36%.

4.7. $[Pt(CH_3CN)_2((S)-MeO-Biphep)][CF_3SO_3]_2$

PtCl₂ ((S)-MeO-Biphep) (60 mg, 7.07×10^{-5} mol) and 38 mg (2.1 equiv.) of AgCF₃SO₃ were mixed in 20 ml CH₃CN solution. The yellow solution remained turbid during the reaction time and a precipitate is formed at a very early stage. The reaction mixture was left to stir overnight under N_2 . The resulting suspension was filtered through a Celite patch via canula, and the CH₃CN removed under vacuum. The yield is quantitative. NMR: ¹H (CD₃CN, 299 K, 700 MHz) 7.77 (ortho-phenyl ring a) 7.65 (m, para-phenyl ring a), 7.47 (meta-phenyl ring a), 7.70 (ortho-phenyl ring b), 7.72 (para-phenyl ring b), 7.66 (meta-phenyl ring b), 6.71 (d, H5). 6.95 (H3), 7.17 (dd,H4), 3.49 (s, OMe), 2.00 (s, CH₃CN); ³¹P (CH₂Cl₂, 299 K, 283 MHz) -1.94 (J_{PPt} 3939 Hz); ¹³C (CH₂Cl₂, 299 K, 176 MHz) 0.5 (CH₃CN) 55.2 (s, OMe), 115.2 (s, C5), 124.8 (m, C3), 129.1 (m, meta-phenyl ring b), 129.2 (m, meta-phenyl ring a), 130.7 (m, C4), 133.1 (s, para-phenyl ring b), 133.4 (s, para-phenyl ring a), 134.8 (ortho-phenyl ring b), 157.8 (quaternary MeO-C); ⁹F (CH₂Cl₂, 299 K, 282.3 MHz) -79.2 (s). MS: 816.7 Pt(CH₃CN)((S)-MeO-Biphep), 775.9 Pt((S)-MeO-Biphep). EA: Calc.: C, 47.48; H, 3.35. Found: C, 47.54; H, 3.36%.

4.8. $[Pt(\mu-Cl)((S)-MeO-Biphep)]_2[BF_4]_2$

PtCl₂((*S*)-MeO-Biphep) (100 mg, 1.18×10^{-4} mol) was dissolved in 10 mL of CH₂Cl₂ in a Schlenk tube under an N₂ atmosphere. To this was added solid AgBF₄ (23 mg, 1.18×10^{-4} mol). After stirring for 3 h, the white-grey solid, observed in the pale yellow solution, was removed via filtration. The solvent is reduced i.v. and the resulting crude product is dried. Yield: 97.5 mg, 92%. NMR: ¹H (CH₂Cl₂, 299 K, 400 MHz) 8.0–6.3 (50 ⁻¹H, aromatic region), 3.45 (12 ⁻¹H, OMe); ³¹P (CH₂Cl₂, 299 K, 161 MHz) 8.74 (*J*_{PPt} 3780 Hz), ¹⁹F (CH₂Cl₂, 299 K, 376 MHz) –152.9 (s).

4.9. [*Pt*(*CH*₃*CN*)₂((*S*)-*MeO*-*Biphep*)][*BF*₄]₂

PtCl₂((*S*)-MeO-Biphep) (50 mg, 5.90×10^{-5} mol) and 24 mg (2.03 equiv.) of AgBF₄ were mixed in 20 mL CH₃CN. The reaction mixture was then stirred for 2 h under N₂. The resulting suspension was filtered over Celite, and the CH₃CN is removed i.v. The crude solid obtained is a mixture of the desired [Pt(CH₃CN)₂((*S*)-MeO-Biphep)][BF₄]₂ and [Pt(μ -OH)((*S*)-MeO-Biphep)][BF₄]₂ as sug-

gested by ¹H and ³¹P NMR. To verify this, an independent sample of $[Pt(\mu-OH)((S)-MeO-Biphep)]_2[BF_4]_2$ was synthesized according to literature [41]. NMR for $[Pt(CH_3CN)_2((S)-MeO-Biphep)][BF_4]_2$: ¹H (CH₂Cl₂, 299 K, 400 MHz) 8.0–6.3 (50 ¹H, aromatic region), 3.53 (12 ¹H, OMe); ³¹P (CH₂Cl₂, 299 K, 161 MHz) –1.69 (*J*_{PPt} 3630 Hz); ¹⁹F (CH₂Cl₂, 299 K, 376 MHz) –152.9 (s).

4.10. $[Pt(\mu-OH)((S)-MeO-Biphep)]_2[BF_4]_2$

Under an N₂ atmosphere; a solution of $AgBF_4$ (27.6 mg, 14.15×10^{-5} mol) in 6 mL of MeOH/H₂O (90/10) was added to a suspension of $PtCl_2((S)-MeO-Biphep)$ (60 mg, 7.07×10^{-5} mol) in 6 mL of MeOH/H₂O (90/10) in a Schlenk tube. The reaction mixture was stirred for 1 h. The resulting suspension was then filtered over Celite and the volume reduced in vacuo to ca. 1 mL. At this point a white crystalline precipitate formed which was recovered by decantation and then washed with several aliquots of cold methanol. The resulting white solid is dried in vacuo. Yield: 47 mg, 2.75×10^{-5} mol, 75%. NMR: ¹H (CH₂Cl₂, 299 K, 300 MHz) 7.38 (ortho-phenyl ring a) 7.18 (metaphenyl ring a), 7.77 (ortho-phenyl ring b), 7.50, 7.62 (metaand para-phenyl ring b), 7.07 (m, H4), 6.72 (m, H3), 6.53 (d, H5), 3.53 (s, OMe), -1.38 (s, (μ -OH)); ${}^{31}P$ (CH₂Cl₂, 299 K, 121 MHz) 1.64 (J_{PPt} 3663 Hz); ${}^{19}F$ (CH₂Cl₂, 299 K, 282.3 MHz) -152.9 (s).

PtCl₂((*R*)-*p*-tol-BINAP), [Pt(μ -Cl)((*R*)-*p*-tol-BINAP)]₂-[CF₃SO₃]₂, and [Pt(CH₃CN)₂((*R*)-*p*-tol-BINAP)][CF₃SO₃]₂ were prepared analogously to the corresponding MeO-Biphep complexes.

4.11. *PtCl*₂((*R*)-*p*-*tol*-*BINAP*)

From PtCl₂(SC₄H₈) (100 mg, 442.3 g mol⁻¹, 2.26×10^{-4} mol) and (*R*)-*p*-tol-BINAP (153 mg, 678.8 g mol⁻¹, 2.26×10^{-4} mol) one obtains 99 mg, Yield: 94%. NMR: ¹H (CH₂Cl₂, 299 K, 300 MHz) 8.00–6.4 (28 ¹H, aromatic region), 2.47 (6 ¹H, Me), 2.04 (6 ¹H, Me); ³¹P (CH₂Cl₂, 299 K, 121 MHz) 8.33 (*J*_{PPt} 3672 Hz); ¹⁹F (CH₂Cl₂, 299 K, 282.3 MHz) –78.2 (s).

4.12. $[Pt(\mu-Cl)((R)-p-tol-BINAP)]_2[CF_3SO_3]_2$

From PtCl₂((*R*)-*p*-tol-BINAP) (100 mg, 10.6×10^{-5} mol), and AgCF₃SO₃ (27.2 mg, 5.29×10^{-5} mol) one obtains 93 mg, Yield: 83%. NMR: ¹H (CH₂Cl₂, 299 K, 300 MHz) 8.0–6.4 (56 ¹H, aromatic region), 2.13 (12 ¹H, Me); ³¹P (CH₂Cl₂, 299 K, 121 MHz) 9.76 (*J*_{PPt} 3663 Hz); ¹⁹F (CH₂Cl₂, 299 K, 282.3 MHz) –78.8 (s).

4.13. $[Pt(CH_3CN)_2((R)-p-tol-BINAP)][CF_3SO_3]_2$

From PtCl₂(*R*)-*p*-tol-BINAP) (50 mg, 5.29×10^{-5} mol) and 28.4 mg (2.1 equiv.) of AgCF₃SO₃ one obtains a quantitative amount of the product as a crude brownish solid. NMR: ¹H (CH₂Cl₂, 299 K, 300 MHz) 8.0–6.5 (56 ¹H, aro-

matic region), 2.52 (6 ¹H, Me), 2.10 (6 ¹H, Me); ³¹P (CH₂Cl₂, 299 K, 121 MHz) -0.8 (J_{PPt} 3675 Hz), ¹⁹F (CH₂Cl₂, 299 K, 282.3 MHz) -78.1 (s).

4.14. X-ray crystal structure

Air stable, light yellow crystals of $[Pt(\mu-Cl){(S)-MeO-Biphep}]_2(CF_3SO_3)_2$, suitable for X-ray diffraction were obtained by crystallization from CH₂Cl₂/hexane. A crystal of the compound was mounted on a Bruker APEX diffractometer, equipped with a CCD detector, for the space group and cell determination and for the data collection.

The space group was determined from the systematic absences, while the cell constants were refined, at the end of the data collection with the data reduction software SAINT [42]. The experimental conditions for the data collection, crystallographic and other relevant data are listed in Table 2 and in Supplementary material.

The collected intensities were corrected for Lorentz and polarization factors [42]. and empirically for absorption using the sADABS program [43]. The structure was solved by direct and Fourier methods and refined by full matrix least squares, [44] minimizing the function $[\sum w(F_o^2 - (1/k)F_c^2)^2]$ and using anisotrospic displacement parameters for all atoms of the cations, except for the hydrogens (see below).

Of the two triflate anions, expected for each dimeric cationic Pt moiety, one was readily found, in general position,

Table 2

Experimental data for the X-ray diffraction study of compound: $[Pt(\mu-Cl){(S)-MeO-Biphep}]_2(CF_3SO_3)_2$

Formula	$C_{78}H_{64}Cl_2F_6O_8P_4Pt_2S_2$		
Formula weight	1892.37		
Data collection $T(K)$	293 (2)		
Diffractometer	Brucker APEX CCD		
Crystal system	orthorhombic		
Space group (No.)	$P2_{1}2_{1}2$ (18)		
a (Å)	26.7954(7)		
b (Å)	30.2583(8)		
<i>c</i> (Å)	9.9179(3)		
$V(\text{\AA}^3)$	8041.3(4)		
Z	4		
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.563		
μ (cm ⁻¹)	37.39		
Radiation	Mo Ka (graphite monochromated,		
	$\lambda = 0.71073 \text{ Å})$		
θ Range (°)	$1.52 < \theta < 26.07$		
Data collected	75471		
Independent data	15871		
Observed reflections (n_0)	13246		
$[F_0 ^2 > 2\sigma(F ^2)]$			
Number of parameters (n_y)	899		
R _{int}	0.0532		
R (observed reflections)	0.0426		
R_w^2 (observed reflections)	0.1097		
Goodness-of-fit	1.001		
Absolute structure parameter	0.000(6)		
(Flack's parameter)			

$$\begin{split} R &= \sum (|F_{o} - (1/k)F_{c}|) / \sum |F_{o}|.\\ R_{w}^{2} &= [\sum w(F_{o}^{2} - (1/k)F_{c}^{2})^{2} / \sum w|F_{o}^{2}|_{2}].\\ \text{GOF} &= [\sum w(F_{o}^{2} - (1/k)F_{c})^{2} / (n_{o} - n_{v})]^{1/2} \end{split}$$

from the Fourier difference maps, and satisfactorily refined anisotropically, even though with the expected large values of the ADP's. However, for each of the two half [Pt(u- $Cl){(S)-MeO-Biphep}]_2$ dimers that form, the asymmetric unit (the dimeric units are generated by a crystallographic binary axis), there is a half $CF_3SO_3^-$ disordered across a crystallographic, but not molecular, binary axis. The resulting disorder is extremely difficult to model. The strongest peaks in the Fourier difference maps were assumed to represents the F, S and O atoms. A model, in which both the CF_3 and SO_3 groups occupy the same positions, with 0.5 occupancy, was constructed and refined with isotropic displacement parameters. Although the resulting geometry could only be very approximate, most of the scattering density is taken into account and the refinement converged satisfactorily. This disorder of the triflates does not affect the geometry of the cations, as this is independent of the model assumed for the refinement.

Upon convergence, the final Fourier difference map showed no significant features. The contribution of the hydrogen atoms, in their calculated position was included in the refinement using a riding model ($B(H) = axB_{(Cbonded)}$ (Å²), where a = 1.5 for the hydrogen atoms of the methyl groups and a = 1.4 for the other hydrogen atoms). No extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature [45]. The handedness of the structure was confirmed by refining the Flack's parameter [46]. All calculations were carried out by using the PC version of the programs: WINGX [47], SHELX-97 [44] and ORTEP [48].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.03.029.

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