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Steric and Electronic Effects in the First Homoleptic Imino Ether Complex: Synthesis and X-ray Crystallographic Determination of $[Pt(NHC(OEt)Et)_4](CF_3SO_3)_2$

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Imino ethers, $NH{=}C(OR')R$, represent an interesting alkoxy-substituted class of otherwise elusive monodentate imine ligands. We have discovered that 4-fold addition of EtOH to $[Pt(N{\equiv}CEt)_4]^{2+}$ proceeds smoothly under basic conditions to yield stable, colorless $[Pt(NH{=}C(OEt)Et)_4]^{2+}(CF_3SO_3^-)_2$ (**1**), *which is the first homoleptic imino ether complex reported for any metal ion*. The monodentate imino ether ligands are all equivalent in solution, according to ^{1}H NMR, and prove to have the *E* isomeric form with *cis* N**H**/C**OEt** groups. The IR-active C−N stretching vibration moves from 2330 cm^{-1} in the nitrile complex to 1633 cm^{-1} in **1**, and ν_{NH} emerges at 3250 cm^{-1}. The ^{195}Pt NMR shift for **1** is found to be −2450 ppm, lying between that for $[Pt(NCEt)_4]^{2+}$ at −2409 ppm and that for $[Pt(NH_3)_4]^{2+}$ at −2580 ppm (all relative to $[PtCl_6]^{2-}$). Single-crystal X-ray diffraction establishes that **1** crystallizes in the monoclinic space group $P2_1/c$, with $a = 9.026(2)$ Å, $b = 14.838$ (1) Å, $c = 13.946$ (1) Å, $\beta = 106.328(2)°$, and $Z = 2$. The metal ion lies at a center of inversion and displays almost ideal square-planar PtN_4 coordination with mean Pt−N distances of 2.016(4) and N−Pt−N angles of 90 ± 0.6°. Within the two crystallographically independent $NH{=}C(OEt)Et$ ligands, the mean N═C distance is 1.283 Å and there is structural evidence of partial π-delocalization of O lone pairs into the NCO moiety. Nonetheless, according to both structural and ^{195}Pt NMR data, the imino ether ligand behaves as innocent Nσ donor toward Pt^{2+}, with a *trans* influence similar to that of Cl$^-$. Due to their extended, asymmetric planar nature, such *E*-$NH{=}C(OR')R$ ligands have exceptional steric requirements which control the coordination geometry and prevent unhindered rotation. These requirements are dominated by alkyl tail-to-tail (R/R) clashes that can be accommodated only by systematic twisting of the ligands about their respective Pt−N bonds. The present study reveals that **1** has the Pt(HHTT) C_{2h} conformation, where H (head up) and T (tail up) represent mutual NH-up and NH-down orientations of the imino ether ligands, with *trans*-ligand pairs cooperatively rotated by about 20° with respect to the PtN_4 plane. The alternative Pt(HTHT) conformer of **1**, with counterrotated *trans* ligands, is predicted to exist independently, possibly in the *chiral* D_2 form, in contrast to unfavored Pt(HHHH).

Introduction

We have discovered that the title compound $[Pt(NHC(OEt)Et)_4](CF_3SO_3)_2$ (**1**) is readily formed as a white solid through exhaustive ethanolysis of $[Pt(EtCN)_4]^{2+}$. Coordinated imino ethers have been known for some time,[1−6] but this is the first report of *homoleptic* complexation for any metal center. Our interest in the nature of bonding in these $NH{=}C(OR')R/Pt^{2+}$ systems is hightened by the consideration that imino ethers represent a distinctive alkoxy-substituted subclass of imine ligands, whereas monodentate imine ligands are otherwise relatively elusive.[7]

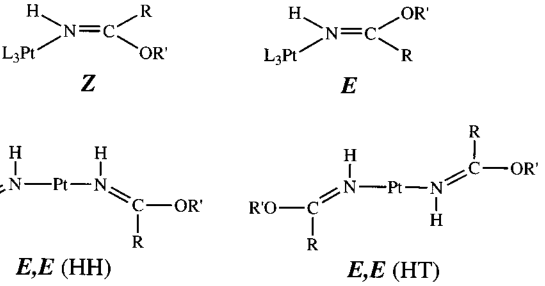

Figure 1. Schematic representation of general platinum−imino ether complexes showing ligands in the *E* conformation and *Z* conformations and mutual head-to-head (HH) and head-to-tail (HT) arrangements. Note that corresponding HH and HT orientations are found in *cis* as well as *trans* isomers.

Imino ether complexes provide a range of important structural possibilities due to the asymmetric and extended nature of the planar ligand.[5,6] The alkoxy imine can adopt either *Z* (*trans*-NH/COR′)[2,3] or *E* (*cis*-NH/COR′)[4,5] geometry (Figure 1). Where both forms are encountered coordinated to Pt(II), the *Z* isomer has been observed to give way to the *E* isomer over time, except when the alkyl substituent (R) is bulky.[5] Attachment of two *E* ligands to a metal center raises further topological complexities—the mutual orientation of the N−H groups in adjacent *E*-type imino ether ligands may be head to head (HH) or head to tail (HT) (Figure 1), where H and T (*i.e.*, head up or tail up, respectively) refer to the NH head group being directed

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Table 1. Crystallographic Data for $[Pt(NHC(OEt)Et)_4](CF_3SO_3)_2$ (**1**)

empirical formula	$C_{22}H_{44}F_6N_4O_{10}PtS_2$
fw	897.81
space group	$P2_1/c$ (No. 14)
temp, °C	23
λ	1.54178
a, Å	9.026(2)
b, Å	14.838(1)
c, Å	13.946(1)
β, deg	106.328(9)
V, Å^3	1792.5(3)
Z	2
ρ_{calc}, g cm^{-3}	1.663
μ_{calc}, cm^{-1}	88.79
R^a	0.023
$R_w{}^b$	0.027

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = \sum w[(|F_o| - |F_c|)^2/\sum(wF_o{}^2)]^{1/2}$.

up or down. In addition, the two imine ligands may of course be located either *cis* or *trans* to one another.

Recently, Cini *et al*. published the structures of *cis*- and *trans*-$[PtCl_2(NHC(OMe)Me)_2]$ (**2** and **3**).[5] They found that the mutual orientation of the imino ether ligands in the *cis* isomer was HT, whereas the HH orientation was found for the *trans* isomer. However, *cis*-$[PtCl_2(NHC(OPr^i)Me)_2]$ (**4**) also has the HH arrangement,[4] in contrast to **2**. The present tetrakis complex, $[Pt(NHC(OEt)Et)_4]^{2+}$ (**1**), provides an instructive comparison since the one coordination center embodies both *cis*- and *trans*-related imino ether ligand pairs and both HH and HT orientations. The relative influence of electronic, steric, and crystal packing effects in these systems can now be judged more reliably, and earlier suggestions can be evaluated in the light of fresh structural and NMR (^{195}Pt) evidence.

Experimental Section

Synthesis of $[Pt(NHC(OEt)Et)_4](O_3SCF_3)_2$ (1). KOH (11.8 mg, 0.21 mmol) was dissolved in 5 mL of freshly distilled ethanol. To this was added under N_2 a solution of 300 mg (0.42 mmol) of $[Pt(EtCN)_4](O_3SCF_3)_2$[8] in 5 mL of ethanol. A white precipitate formed almost immediately; however, stirring was continued for 3 h. The analytically pure solid was filtered off, washed with 2 × 2 mL ether, and sucked dry. Yield: 287 mg (76%). Anal. Calcd for $C_{22}H_{44}F_6N_4O_{10}PtS_2$: C, 29.4; H, 4.9; N, 6.2. Found: C, 29.5; H, 5.3; N, 6.0. ^{1}H NMR ($CDCl_3$; ppm): 1.17, (t, J = 7.6 Hz, $CH_3CH_2C{=}N$), 1.34, (t, J = 7.0 Hz, CH_3CH_2O), 2.89, (q, J = 7.6 Hz, $CH_3CH_2C{=}N$), 4.12, (q, J = 7.0 Hz, CH_3CH_2O), 8.08, (s (br), NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$; ppm): 10.49 ($CH_3CH_2C{=}N$), 13.60 (CH_3CH_2O), 29.19 ($CH_3CH_2C{=}N$), 65.04 (CH_3CH_2O), 120.41 (J_{CF} = 319 Hz, $CF_3SO_3^-$), 176.42 ($^2J_{PtC}$ = 35 Hz, C=N). ^{195}Pt NMR ($CDCl_3$; ppm): −2450, consistent with a $Pt^{II}N_4$ complex (*cf*. $Pt(EtCN)_4{}^{2+}$ δ_{Pt} −2409[9]). IR (KBr; cm^{-1}; values in italics correspond to lattice $CF_3SO_3^-$): 3250 (m), 2993, 2948, 2884 (all weak), 1633 (strong), 1473, 1458, 1442, 1400 (m), 1380 (weak), *1272*, 1246, *1225*, *1158* (strong), 1117, 1089 (m), *1033* (strong), 1003, 909, 865, 822, 757 (weak), *640* (m), *574*, *518*, 477 (weak). LSIMS mass spectrum: m/z 747.9; $[Pt(NHC(OEt)Et)_4](O_3SCF_3)^+$ requires m/z = 748.3.

X-ray Crystallography. A colorless block of **1** grown from CH_2Cl_2 solution by slow evaporation and mounted on a quartz fiber was examined by Cu Kα radiation, with a Rigaku AFC6R rotating-anode diffractometer (Table 1). All calculations were performed with the teXsan software package.[10] The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques.[11] Non-hydrogen atoms were refined anisotropically; H(−N) atoms were located from difference maps and not refined; H(−C) atoms were similarly located then fixed in idealized positions, setting H−C = 0.95 Å, $U(H) = 1.2U_{eq}(C)$. Neutral-atom scattering factors were taken from Cromer and Waber.[12] Crystal decay was limited to 4.9%. Semiempirical absorption corrections, consistent with the small, regular nature of the crystal, were based on azimuthal (ψ) scan data.[14] The final cycle of full-matrix least-squares refinement was based on 2301 observed reflections ($I > 3.00\sigma(I)$) and 294 variable parameters.

Other Physical Measurements. Routine ^{1}H and ^{13}C NMR spectra of **1** between 223 and 323 K in $CDCl_3$ were recorded on a Varian Gemini 300 spectrometer, with chemical shifts referred to solvent proton and carbon resonances (7.25 ppm for ^{1}H and 77.0 ppm for ^{13}C). ^{195}Pt NMR spectra (15.5 μs pulse (90°), acquisition time 150 ms, delay 300 ms) were recorded on a Varian XL 200 spectrometer with a 5 mm probe and referred to external $PtCl_4{}^{2-}$ (−1630 ppm). IR spectra, 4000−400 cm^{-1}, were recorded on a Perkin-Elmer 1600 FTIR spectrometer. The LSIMS spectrum was recorded on a Fisons Instruments VG-ZAB2-SEQ mass spectrometer using a cesium ion gun operating at 30 kV with a m-nitrobenzyl alcohol matrix. Elemental microanalyses were performed within this institution.

Results and Discussion

Base-assisted EtOH addition to the four Pt−NCEt moieties results exclusively in *E* stereochemistry (Figure 1) about each C=N bond to form the stable, colorless tetrakis (imino ether) complex. ^{1}H NMR spectra confirm that in solution all four ligands are equivalent, with just two sets of distinguishable ethyl resonances (N=C−Et and O−Et). The infrared-active C−N stretching vibration shifts from 2330 cm^{-1} in $Pt(EtCN)_4{}^{2+}$ to 1633 cm^{-1} in **1**, and ν_{NH} emerges at 3250 cm^{-1}. The NMR data will be discussed in more detail below, after further consideration of the structure.

Pertinent interatomic bond lengths and angles for compounds **1**−**4** are compared in Table 2. The present geometric data are distinctly more precise than for the structures studied previously. An ORTEP[13] perspective view of the cation is shown in Figure 2. The platinum atom of **1** lies on a center of inversion, coordinated to two pairs of crystallographically independent imino ether ligands. The center of inversion leads to the two-up two-down, HHTT, conformation. The Pt−N(11) and Pt−N(21) bond lengths are experimentally indistinguishable (mean value 2.016 Å) in the crystal, and the N−Pt−N angles are close to 90° (Table 2), leading to almost ideal square-planar coordination.

Spatial models of **1** in various conformations confirm that mutual steric interference is a real possibility due to alkyl/alkyl (R/R) tail-to-tail clashes between ligands of the same orientation (*i.e.*, HH *or* TT). This applies equally for both *cis* and *trans* pairs of ligands. If two *trans* ligands were closely confined to a common plane (for example, both perpendicular to the PtN_4 plane), then the HH arrangement would certainly be strongly

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Table 2. Comparison of Selected Bond Lengths and Angles for Structurally Characterized Pt−Imino Ether Complexes

bond length (Å) or angle (deg)[a]	**1**	**2**[b]	**3**[b]	**4**[c]
Pt−N	2.020(4) 2.013(4)	2.010(8)	1.989(7) 2.009(8)	2.013(7) 2.020(7)
Pt−Cl		2.303(3)	2.298(2) 2.301(2)	2.31(2) 2.32(2)
N=C	1.274(5) 1.286(5)	1.273(12)	1.307(11) 1.273(12)	1.269(11) 1.282(12)
C−O	1.322(5) 1.327(5)	1.327(12)	1.315(11) 1.306(11)	1.340(11) 1.328(11)
Pt−N=C	128.1(3) 128.6(3)	126.4(7)	125.6(6) 126.7(7)	128.7(6) 127.0(6)
N=C−C$_1$	122.7(4) 122.2(4)	123.3(9)	122.2(8) 123.7(8)	123.1(8) 122.3(8)
N=C−O	125.1(4) 124.2(4)	125.2(8)	124.4(8) 125.1(9)	125.6(8) 124.8(8)
O−C−C$_1$	112.2(4) 113.8(4)	111.3(8)	113.4(8) 111.1(8)	111.3(7) 112.6(8)
N−Pt−N	90.6(1) 89.4(1)	89.4(5)	179.1(2)	88.30(28)

[a] Labeling scheme is as follows: PtN=C(OR′)C$_1$. [b] From ref 5. [c] From ref 4.

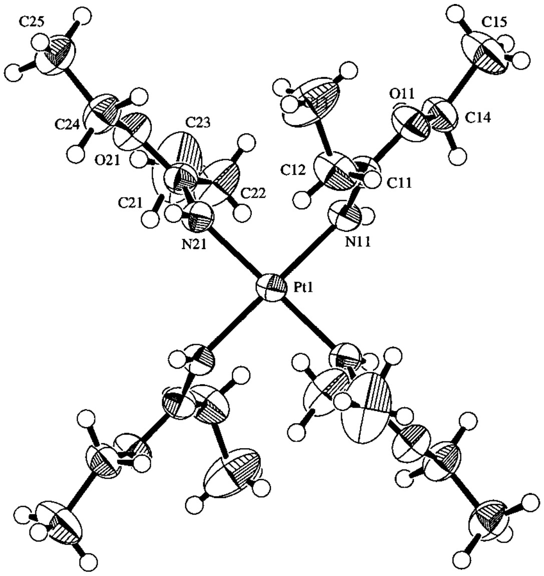

Figure 2. ORTEP view of [Pt(NHC(OEt)Et)$_4$]$^{2+}$ from **1** showing the atom-numbering scheme and 30% probability ellipsoids.

unfavored and probably impossible, even for R = Me. This is equally true for two *cis* ligands confined strictly perpendicular to the PtN$_4$ plane. So the question of possible coordination structures is really a question of the freedom of each ligand to rotate about its Pt−N bond so as to relieve the tail-to-tail clash. Figure 3 shows the nature of three conceivable structures for the homoleptic complex and their idealized symmetries: (a) Pt(HHHH), (b) Pt(HHTT), and (c) Pt(HTHT), disregarding irrational Pt(H$_3$T). In structure a, no combination of Pt−N rotations can alleviate the multiple tail-to-tail clashes. Structure b imposes two *cis* tail-to-tail clashes, while structure c imposes two *trans* tail-to-tail clashes. In the case of structure b, the mutual rotations shown along each N−Pt−N axis (maintaining the coplanarity of *trans*-related HT ligands) reduce the *cis* tail-to-tail clash. In the case of structure c, opposing twists about the *trans* N-Pt and Pt−N′ bonds (as shown in Figure 3) relieve the *trans* tail-to-tail clash along that N−Pt−N′ axis, and this needs to be repeated along the other N−Pt−N′ axis. Routine NMR spectra could not in themselves establish the true arrangement in the first instance, since the four ligands are mutually equivalent in each case. The present crystal structure determination was necessary to settle the issue, revealing structure b for **1** as presently isolated. The dihedral angles between the PtN$_4$ coordination plane and the ligand planes defined by N(11)O(11)C(11)C(12) and N(21)O(21)C(21)C(22) are 75.3 and 67.6°, respectively, with the R groups rotated *away* from each other as shown in Figure 3b. These deflections are evident on close examination of Figure 2, which has the same orientation.

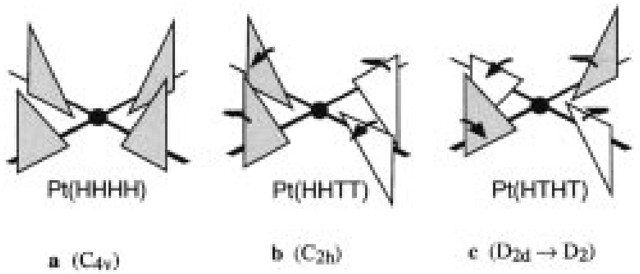

Figure 3. Schematic diagram showing possible orientations of imino ether ligands in the homoleptic complex. Also shown are Pt−N rotations which reduce tail-to-tail clashes implicit in HH (or, equivalently, TT) ligand-pair relationships. The point group of Pt(HTHT) would be D_{2d}, rather than D_2, if the ligands remained vertical (*i.e.*, untwisted).

While the crystallographic distinction between the N(11) and N(21) ligands is naturally lost in solution, spatial models suggest that mutual steric hindrance precludes full rotation of a given ligand about its Pt−N bond. Thus, we believe the center of inversion observed in the solid state structure of **1** is preserved and it achieves true C_{2h} symmetry when it dissolves. In accord with this, ^{1}H NMR studies in the range 223−323 K show no sign of conformational exchange, and **1b** is recovered unaltered after the high-temperature cycle. Examination of models for **2**−**4** shows that alkyl tail/chloride coligand interactions seriously hinder free rotation of the imino ether ligands with respect to the coordination plane in the bis(imino ether) compounds as well.

The ligand/ligand relationships uncovered here permit a more enlightened appreciation of earlier structures. For example, the *cis*-bis(imino ether) complexes of stoichiometry PtCl$_2$L$_2$ crystallize in contrasting HT (**2**)[5] and HH (**4**)[4] arrangements, with differently organized NH···Cl H-bonding networks. As stressed above, the configuration observed in **1** (where both *cis*-HH and *cis*-HT interactions can be studied simultaneously) establishes there is no hindrance to the head-to-head arrangement for a pair of *cis* imino ether ligands if they are suitably rotated to relieve the tail-to-tail congestion. On inspection, we find the *cis*-HH ligands in **4** show mutually opposed rotations (+13°, −15°) from the vertical, whereas the single pair of *cis*-HT ligands in **2** remain almost perpendicular to the PtN$_4$ plane, since they lack a tail-to-tail clash (they are actually rotated +8° in the *same sense*).

There is an equally instructive contrast between the *trans*-related ligand pairs found in **1** and **3**. In **1**, as shown in Figure 3b, HT-related *trans* imino ether ligands occupy the same plane without hindrance (satisfying the crystallographic center of inversion at Pt), whereas in **3** the opposed HH *trans* imino ether ligands rotate significantly (+16°, −22°) to relieve the potential tail-to-tail clash. Thus **3** serves as a model for the *trans*-ligand relationships in the feasible but as yet uncharacterized HTHT isomer of **1** (Figure 3c). We conclude the more specific steric and electronic factors invoked previously[5] are not required to explain the range of observed behavior in compounds **1**−**4**.

The extended planarity of the imino ether ligands incorporating the methoxy carbon atom is a notable feature of **2** and **3**.[5] This is approximately preserved in **1**, with C(14) and C(24) lying 0.13 and 0.21 Å from the respective N=C−O planes,

Table 3. ^{195}Pt NMR Data for $Pt^{II}N_4$ Complexes

complex	δ_{Pt}[a]	ref
Pt(TMTAA)[b]	−2048	9
cis-$Pt(NH_3)_2(NO_2)$	−2214	17
$Pt(EtCN)_4^{2+}$	−2409	9
$Pt(NHC(OEt)Et)_4^{2+}$ (**1**)	−2450	this work
$Pt(NH_3)_4^{2+}$	−2580	17
Pt(TPP)[c]	−3287	18
$Pt(C_8doH)_2$[d]	−3371	9

[a] Chemical shifts in ppm relative to $PtCl_4^{2-}$ = −1630 ppm. [b] TMTAA = 5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclodecinate(2−). [c] TPP = 1,5,10,15-tetraphenylporphinate(2−). [d] C_8doH = cyclooctane-1,2-dioximate(1−).

perhaps due to the greater steric demand of OEt *vs* OMe. The measured torsion angles are 6.1(7) and 9.6(6)° for N(11)C(11)-O(11)C(14) and N(21)C(21)O(21)C(24), respectively, for the atoms labeled as in Figure 2. Restricted rotation is consistent with partial π-delocalization of the oxygen atom lone pairs,[5] a suggestion confirmed in our view by the distinctive contraction of the =C−O bond (Table 2) to a value intermediate between conventional single- and double-bond lengths. In the low-temperature ^{1}H NMR studies of **1** in $CDCl_3$, there is evidence at 223 K for the selective onset of retarded motion specific to the O−Et groups.

Detailed comparisons of the bond lengths and angles among the four compounds are necessarily restricted, since the nominal differences within Table 2 lie within or close to the 3σ error margins for **2**−**4**. Nevertheless, some general features emerge. The internal geometries appear quite similar overall, despite the differing number and disposition of NH=C(OR′)R ligands, the alternative Et (**1**) or Me (**2**−**4**) R groups, and the increasing bulk of the OR′ function with −OMe (**2**, **3**) < −OEt (**1**) < −O^{i}Pr (**4**). Table 2 reveals a consistent pattern in the nominally trigonal (sp^2) bond angles, as follows: (i) Pt−N−C and N−C−C_1 are *ca.* 127 and 123°, respectively; (ii) N−C−O is *ca.* 125°; and (iii) C_1−C−O is correspondingly diminished, quite sharply, to 112°. Cini *et al.* argued[5] that steric interactions are important in this context, attributing (i) to possible Pt···alkyl clashes and (ii) to repulsive alkoxy−CH···NH interligand contacts. The lack of systematic dependence on the nature of R and R′ seems to undermine this explanation. A similar, apparently intrinsic, pattern of bond angles is found even in free (uncoordinated) imino ethers and in related organic compounds containing an *E*-configured R″N=C(OR′)R moiety.[6,15]

The Pt−N bond lengths appear to be approximately the same whether the imino ether ligand is *trans* to Cl^- or to another imino ether group, implying that the imino ether and the halide have a similar *trans* influence (as borne out by NMR studies; see below). In addition, Pt−N bond lengths of *ca.* 2.01 Å (Table 2) are comparable with those in *cis*-$PtCl_2(NH_3)_2$,[16] with "innocent" σ-donor ammine ligands. This suggests that platinum/imino ether π interactions are negligible.

We have turned to NMR spectroscopy for further insight into the nature of the Pt(II)/imine bond in **1**. Table 3 lists ^{195}Pt NMR data for several platinum(II) complexes with four nitrogen donors.[17,18] There is a remarkable spread of values for δ_{Pt} of over 1300 ppm which is difficult to rationalize within the current theory of ^{195}Pt shifts. Metalla-ring strain may play a part, as shown by comparison of $[Pt(NH_3)_2(\mu\text{-}OH)]_2^{2+}$ (δ_{Pt} −1100), where the two Pt atoms are contained in a four-membered ring, and *cis*-$[Pt(NH_3)_2(OH)_2]$ (δ_{Pt} −1500).[19] Another contribution to the wide variation in Table 3 may be differing proportions of σ and π characters in the Pt−N bond, leading to changes in the shielding of the platinum nucleus. The chemical shift of **1** (−2450 ppm) is similar to those of $[Pt(NH_3)_4]Cl_2$ (−2580 ppm) and $[Pt(EtCN)_4]^{2+}$ (−2409 ppm). This is a further sign that π-bonding of imino ether ligands with Pt(II) is insignificant, since ammines are σ-only donors and since nitrile ligands are apparently comparable with Cl^- in their π-bonding properties (*i.e.*, weakly π-donating rather than π-accepting) on Ru(II) and Ru(III) sites.[20]

Independent evidence of the electronic character of imino ether ligands can be gleaned from comparison of platinum coupling constants.[21] Thus for *trans*-$[Pt(CF_3)Cl(PMe_2Ph)_2]$, $^2J(Pt-CF_3)$ = 757 Hz, while for a series of *trans*-$[Pt(CF_3)L(PMe_2Ph)_2]^+$ analogues (where L = ArCN, *HN=C(OMe)C*$_6$*F*$_5$, pyridine, EtNC) $^2J(Pt-CF_3)$ = 778, *724*, 702, and 662 Hz, respectively. This suggests that imino ethers have only moderate *trans* influence, akin to chloride and arenenitriles.

Two final comments on the general ^{1}H NMR characterization of imino ether ligands are warranted. For a range of $PtCl_2(NH=C(OMe)R)_2$ complexes, Cini *et al.*[5] established a consistent distinction in the ^{1}H NMR of *E* and *Z* forms of the ligand, with opposing shifts in R and OR′ signals. For example, with R = Et and OR′ = OMe, the measured shifts were OCH_3 = 3.83 ppm and N=C−CH_2− = 3.19 ppm for the *E* form *vs* OCH_3 = 4.65 ppm, N=C−CH_2− = 2.48 ppm for the *Z* form. However, in homoleptic **1**, containing exclusively *E* ligands, the corresponding shifts for the methylene groups, −O−CH_2− (4.12 ppm) and N=C−CH_2− (2.89 ppm), are intermediate between those listed above for Cini's *E* and *Z* forms. Thus, prior to the X-ray determination, the evident stability of **1** was the only circumstantial indication of its favored ligand geometry (*E*). Interestingly, the OEt and N=CEt resonances are conveniently differentiated in **1** by their precise J_{HH} values (7.0 and 7.6 Hz, respectively), which coincide with the values in the EtOH and $Pt(EtCN)_4^{2+}$ precursors.

Conclusions

Complex **1** is the first example of a new family of stable, colorless tetrakis(imino ether) platinum(II) complexes. The extended planar nature of the ligands (L) determines the conformational possibilities in planar MX_2L_2 and ML_4 systems through ligand/ligand steric demand. With reference to their interesting status as alkoxy-substituted monodentate imine ligands, imino ethers appear to function as innocent σ-donors toward planar Pt(II) on the basis of both structural and electronic evidence. This aspect of their behavior should be re-examined for contrasting situations such as octahedral Ru^{2+} (π-donor) and Ru^{3+} (π-acceptor) binding sites.

The solvato complex $[Pt(EtCN)_4]^{2+}$ has promise as a convenient and versatile starting material,[8] but it would be as well to remember its tendency to react with alcohols, especially under basic conditions. Studies are continuing on the exhaustive alcoholysis of a range of $[Pt(RCN)_4]^{2+}$ complexes. We predict the existence of a conformer of $Pt(NHC(OR')_4^{2+}$ with a Pt(HTHT) arrangement (*cf.* Figure 3c) displaying a uniform

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ligand inclination of *ca*. 15−20°, and therefore chiral (D_2). For example, it should be possible to convert Cini's *trans* bis-HH complex (**3**) to *trans*-[Pt(MeCN)$_2$(NHC(OMe)Me)$_2$] and then to homoleptic [Pt(NHC(OMe)Me)$_4$] in the HTHT form.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure of [Pt(NHC(OEt)Et)$_4$](O$_3$SCF$_3$)$_2$ (**1**) is available on the Internet only. Access information is given on any current masthead page.

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