Rhenium, Palladium, and Copper Pyridylalkoxide Complexes: Synthesis, Structural Characterization, and Catalytic Application in Epoxidation Reactions

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Reaction of bis(alkyl/aryl)-2-pyridylalcoholate ligands (**a**−**g**) with $[ReOCl_4](NBu_4)$ results in the formation of metal-oxo complexes of the general formula $[ReOCl_3(L)](NBu_4)$ (**2**, **3**) and $[ReOCl(L)_2]$ (**4**, **5**), with L = bis(alkyl/aryl)-2-pyridylalcoholate. Molecular structures of the complexes **2a**, **4a**, and **5a** have been determined by single-crystal X-ray diffraction studies. Besides the expected crystal structure of **4a**, where an alkoxide site of one of the ligands is coordinated trans to the rhenyloxo fragment, complex **5a** shows a rare example of a trans chloro-oxo $[ReOCl(L)_2]$ connectivity. Additionally, starting from $Pd(OAc)_2$ and $[CuCl_2{\cdot}2(H_2O)]$ complexes of the form $[M(L)_2]$ (M = Cu, Pd) (**6a**−**g** and **8a**) were prepared. For complexes **6a** and **8a** molecular structures have been determined by single-crystal X-ray diffraction studies, which showed the expected square planar geometry with the pyridine ring nitrogens situated mutually in trans position. Complexes **3**, **4**, **6**, and **8** were tested in the epoxidation reaction of cyclooctene with TBHP (*tert*-butylhydrogenperoxide).

Introduction

Recently we reported the synthesis of new oxovanadium(IV) complexes of the type $[VO(L)_2]$ (L = 2-pyridinyl alcoholate) as catalysts for olefin epoxidation.[1] These pyridinyl alcohols have proven to be universal ligands for highly active epoxidation catalysts based on the early transition metals Mo, Ti, V, and W.[1,2] Other ligand systems are known to catalyze olefin epoxidation reactions,[3−6] but 2′-pyridinyl alcoholate ligands are considered superior because they can be easily prepared with broad variation. This has already been demonstrated for various 2′-pyridinyl alcoholates bearing aryl or alkyl moieties, respectively.[7−10] Another important advantage of these ligands is their strong resistance toward degradation, which is crucial for their application in oxidation catalysis.[11]

Because of the enormous current interest in Mo- or W-based epoxidation catalysts bearing a bischelating 2′-pyridinyl alcoholate ligand, examples of rhenium,[12−14] copper,[15−17] and palladium[17,18] complexes with this ligand type are still rare. The objective of further research was to develop an easy and straightforward method for the synthesis of rhenium, palladium, and copper complexes and to investigate their potential as epoxidation catalysts.

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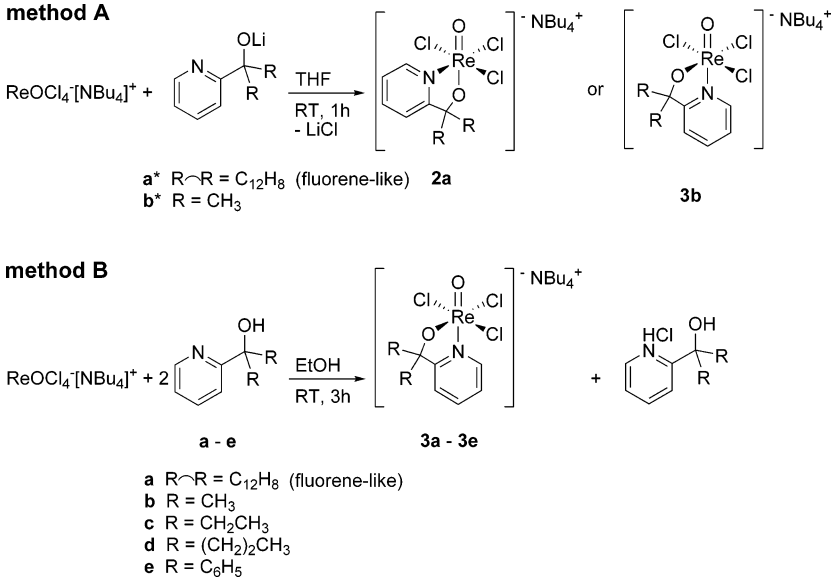
Scheme 1. Synthesis of Complexes 2a, 3a−e via the Salt Route (Method A) and the Free Ligand Route (Method B)



Results and Discussion

Oxorhenium(V) Complexes. More than 10 years ago the field of oxorhenium(V) complexes was almost exclusively limited to adducts of the [$ReOCl_3$] fragment.[19] The first advances in catalytically relevant Re(V) compounds were published by Herrmann and Rauch in 1996: reacting [$ReOCl_4$](NBu_4) with salen and bidentate Schiff-bases, respectively, the complex types [ReOCl(L)] and [$ReOCl(L)_2$] were developed.[20] By adapting Jacobsen's manganese(V)−salen synthesis,[5] active catalysts for epoxidation were obtained, irrespective of whether bi- or tetradentate ligands were used. As the resulting [$ReOCl_3$(L)](NBu_4) (L = N,O-chelating ligand) type complexes are still rare,[21] the preparation of Re(V)-pyridinyl alcoholate complexes of the form [$ReOCl_3$(L)](NBu_4) and [$ReOCl(L)_2$] was the main focus of this work.

Three convenient rhenium(V) precursors for ligand exchange reactions predominate in the literature: [$ReOCl_4$](NBu_4) (**1**),[22] [$ReOCl_3(PPh_3)_2$],[23] and [$ReO(CH_3)Cl_2$(4-*tert*-butylpyridine)$_2$].[24] We obtained no substitution reactions with the complexes [$ReOCl_3(PPh_3)_2$] and [$ReO(CH_3)Cl_2$(4-*tert*-butylpyridine)$_2$] with our pyridinyl alcoholate ligands, in contrast to Bandoli and Gerber,[14a] where di-(2-pyridyl)ketone ligands were used. On the other hand, [$ReOCl_4$](NBu_4) was found to be an excellent starting material for the substitution reaction using pyridinyl alcoholate ligands. Two methods are possible for the preparation of the [$ReOCl_3$(L)](NBu_4) type complexes **2** and **3** (Scheme 1).[7]

In method A (salt method) complex **1** reacts with the corresponding lithium salt (**a***, **b***) of the pyridinyl alcohol (**a**, **b**) in THF. During the reaction 1 equiv of lithium chloride is formed and can be precipitated by addition of *n*-hexane. The desired complex was then obtained by recrystallization from methylene chloride.

Method B was found to be much more convenient; in this case, complex **1** is dissolved in dry ethanol or THF and 2 equiv of the pyridinyl alcohol (**a**−**e**) is added at room temperature. During a short period of time (∼30 min) the desired complex precipitates quantitatively from the ethanol solution. The second equivalent of the pyridinyl alcohol acts as a base and forms a hydrochloride salt with the formed HCl. An attempt to use triethylamine instead of a second equivalent of the pyridinyl alcohol resulted in decomposition of the starting material. The main advantage of method B is that no lithium chloride is formed; alleviating the need for its removal from the reaction mixture. The formed hydrochloride in method B remains in solution and was separated by filtration to obtain the rhenium

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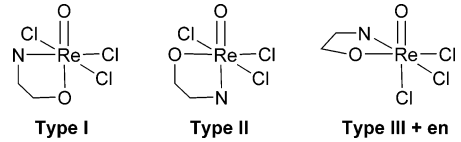


Figure 1. Possible orientations for a [$ReOCl_3(L)$] complex (en = enantiomer).

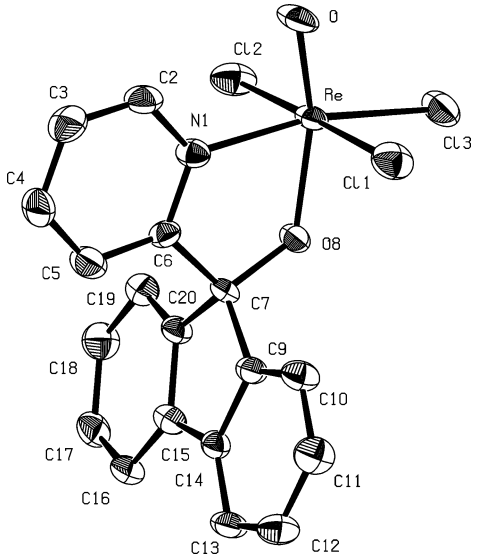
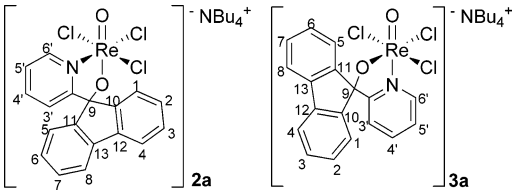


Figure 2. ORTEP style representation of the molecular structure of the anionic part of complex **2a** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Re−Cl1, 2.419(2); Re−Cl2, 2.409(2); Re−Cl3, 2.347(2); Re−O, 1.681(5); Re−O8, 1.946(3); Re−N1, 2.142(5); O8−C7, 1.412(6); Cl1−Re−Cl2, 177.75(6); Cl3−Re−O, 104.5(2); Cl3−Re−N1, 167.9(1); O−Re−O8, 162.8(2); O8−Re−N1, 75.2(2); Re−O8−C7, 126.3(3).

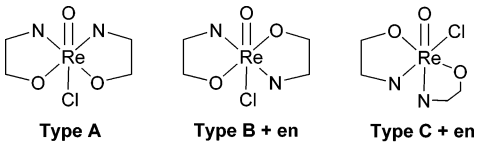
Table 1. Comparison of the ^{1}H NMR Spectra of Complexes 2a and 3a in d_6-DMSO



proton	δ [ppm] **2a**	δ [ppm] **3a**
H6′	8.18 (1H, d)	9.12 (1H, d)
H1/5	7.89 (2H, d)	8.28 (2H, d)
H4/8	7.79 (2H, d)	7.70 (2H, dd)
H4′	7.59 (1H, dd)	8.62 (1H, dd)
H3/7	7.36 (2H, dd)	7.85 (2H, dd)
H5′	7.32 (1H, dd)	8.24 (1H, dd)
H2/6	7.16 (2H, dd)	7.76 (2H, d)
H3′	6.57 (1H, d)	7.58 (1H, d)

complexes as pure solids. By these two synthetic routes, the complexes **2a**, **3a**−**e** were prepared in high yields.

Complexes **2a**, **3a**−**e** were characterized by IR spectroscopic methods, elemental analysis, NMR spectroscopy, and, for **2a**, by solid-state X-ray analysis. In each case, the IR spectrum confirms the presence of a Re═O fragment, with a stretching frequency between 940 and 995 cm^{-1}.[13,14a,25,26] Furthermore,



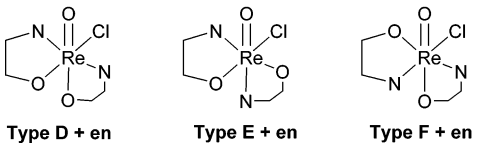
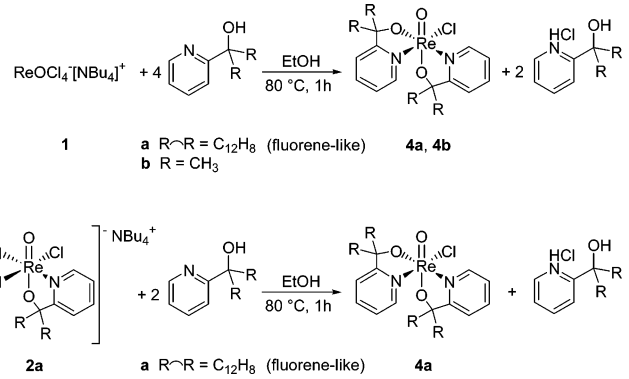


Figure 3. Possible orientations for a [$ReOCl(L)_2$] complex (en = enantiomer).

Scheme 2. Synthesis of Neutral Bis(pyridylalkoxy)rhenium Complexes



in these complexes the strong band in the aromatic region confirms the presence of the ligand. The elemental analyses reflect unambiguously the basic formula of [$ReOCl_3(L)$](NBu_4) for each complex.

In principle there are three geometric possibilities (type I−III) for the coordination of a bidentate N,O-ligand to a [$ReOCl_3$] fragment (Figure 1). Unambiguous determination of which of these three possibilities a certain complex adopts is only possible by solid-state X-ray analysis. However, by correlating the generated X-ray structures with the NMR data, we can present tentative assignments of the likely connectivity for complexes where X-ray data were not obtained. Complex **2a** was prepared according to the salt method (a), and a solid-state structure is depicted in Figure 2. Crystal data and details of the structure determination are summarized in Table 4.

According to Figure 2 the prepared complex **2a** shows the structure type I, where all three chloro ligands are coplanar and the oxygen of the pyridine ligand is coordinated trans to the oxo ligand of the rhenium. The rhenium atom shows a pseudo-octahedral coordination environment with a substantial distortion (O−Re−O8, 162.8(2)°). The Re═O bond distance (1.681(5) Å) is in agreement with known complexes in the literature.[13,27,28]

Our question was now is it possible to obtain also complexes with a structure of type II or III? Toward this goal the second synthesis route, via the free ligand, plays an important role in the preparation of complexes of type II and III. If complex **1** reacts with ligand **a** in THF, a light green powder of complex **3a** is obtained, which shows a dramatically different ^{1}H NMR spectrum from complex **2a** (Table 1).

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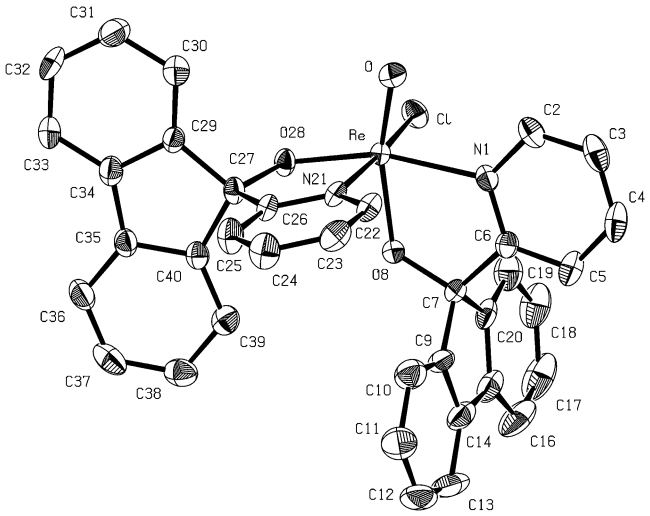
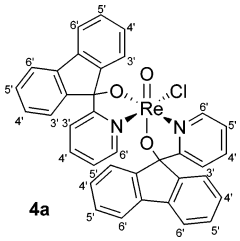


Figure 4. ORTEP style representation of the molecular structure of complex **4a** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Re−Cl, 2.392(1); Re−O, 1.696(3); Re−O8, 1.966(3); Re−O28, 1.933(2); Re−N1, 2.161(3); Re−N21, 2.110(3); O8−C7, 1.418(5); O28−C27, 1.432(4); Cl−Re−O, 94.4-(1); Cl−Re−N21, 171.23(8); O−Re−O8, 161.3(1); O−Re−O28, 110.1(1); O8−Re−N1, 74.8(1); O8−Re−N21, 85.7(1); O28−Re−N1, 162.2(1); O28−Re−N21, 81.0(1); N1−Re−N21, 95.6(1); Re−O8−C7, 125.6(2); Re−O28−C27, 118.6(2).

Table 2. H,H-DQF-COSY and H,C-HSQC NMR Correlation of Complexes 4a in d_6-DMSO



	H6′	H5′	H4′	H3′
pyridine ring 1	8.97	7.53	7.89	6.70
pyridine ring 2	8.69	7.82	8.07	7.09
phenyl ring 1	7.91	7.24	7.44	6.99
phenyl ring 2	7.89	6.86	7.31	6.18
phenyl ring 3	7.89	6.66	7.26	6.88
phenyl ring 4	7.89	7.37	7.19	7.89

The comparison of the NMR spectra of complexes **2a** and **3a** show that these two compounds cannot be structurally equal. For instance, the signal for the H6′-atom in complex **3a** is located much more downfield than that of **2a** at a chemical shift of 9.12 ppm. This signal suggests the structure type II for complex **3a** (Table 1), where the pyridinyl group is coordinated trans to the oxo ligand, based on literature examples of type II complexes in which the H6′-atom has a chemical shift between 8.6 and 9.2 ppm.[26,29]

Variable-temperature NMR measurements were carried out on complex **2a** to determine which complex (**2a** or **3a**) is the more configurationally stable of the pair and whether interconversion was possible. Above 80 °C a new signal set was formed quantitatively, which showed no reversibility after cooling the NMR tube to room temperature. In this case a strong downfield chemical shift for the pyridine proton at the C6′ carbon was observed, which might result from the fact that the nitrogen atom of the pyridine ring is no longer coordinated trans to a chloro ligand (**2a**), and is instead now trans to the oxo ligand

Table 3. Selected Bond Distances (Å) and Torsion Angles (deg) for the Complexes 6a (M = Pd) and 8a (M = Cu)

	6a	8a
M−O8	1.994(2)	1.912(2)
M−N1	1.993(3)	1.961(2)
N1−C6	1.355(4)	1.346(3)
C6−C7	1.536(4)	1.536(3)
O8−C7	1.399(3)	1.401(2)
O8−M−N1	82.48(9)	84.38(6)
O8−M−N1	97.52(9)[a]	95.62(6)[b]
M−N1−C6	113.5(2)	113.0(1)
N1−C6−C7	113.9(2)	113.5(2)
O8−C7−C6	110.1(2)	109.3(2)
M−O8−C7	110.4(2)	112.5(1)

[a] Symmetry code for equivalent atoms (1 − x, 1 − y, 1 − z). [b] Symmetry code for equivalent atoms ($^2/_3$ − x, $^1/_3$ − y, $^1/_3$ − z).

(**3a**) (Table 1). With this experiment, complexes of type I were specified as the kinetic products, which can be thermally isomerized to the thermodynamically more stable product of type II. Using both synthetic routes, only one product was formed in the case of ligand **b**. Ligand **a** seems to be a special case for the observation of both complex types (I and II) under the chosen reaction conditions.

After the structural classification of complexes of the type $[ReOCl_3(L)](NBu_4)$, we were interested in investigating the synthesis of $[ReOCl(L)_2]$ type complexes and their structural configuration. These complexes were obtained starting from $[ReOCl_4](NBu_4)$ (**1**) or $[ReOCl_3(L)](NBu_4)$ (**2a**) by the addition of 4 equiv or 2 equiv of 2′-pyridinyl alcohol, respectively (Scheme 2).

During the reaction at room temperature the initial anionic complex of type $[ReOCl_3(L)](NBu_4)$ precipitates from the ethanol solution. Afterward the solution was heated to reflux, at which point the original precipitate redissolves, and a light green solid precipitates from the reaction mixture after approximately 30 min (Scheme 2).

Full characterization of the $[ReOCl(L)_2]$ type complexes **4** was carried out with complex **4a** to obtain experimental data analogous to the $[ReOCl_3(L)](NBu_4)$ complexes **2** and **3**, for the determination of the coordination mode of two bischelating N,O ligands coordinated at the ReOCl fragment. As for the $[ReOCl_3(L)](NBu_4)$ complexes (**2**, **3**), there are a number of different possible orientations for the ligands in a $[ReOCl(L)_2]$ type complex, which are shown in Figure 3. Two subgroups are possible, where the chloro ligand is coordinated trans (type A and B), or cis to the Re═O group (type C−F) (Figure 3).

For complex type A no enantiomers exist because of the plane of symmetry in the molecule. However, including types B−F and their corresponding enantiomers, there are eleven different structures possible for this complex (**4**). The most common structure types for $[ReOCl(L)_2]$ complexes with Schiff-base ligands are type D and F complexes, where the oxygen atom of one of the ligands is coordinated trans to the oxo ligand.[13,28,30]

(29) (a) Mayer, J. M.; Tulip, T. H.; Calabrese, J. C.; Valencia, E. *J. Am. Chem. Soc.* **1987**, *109*, 157. (b) Takacs, J.; Kiprof, P.; Kuchler, J. G.; Herrmann, W. A. *J. Organomet. Chem.* **1989**, *369*, C1. (c) Herrmann, W. A.; Kuchler, J. G.; Weichselbaumer, G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989**, *372*, 351. (d) Takacs, J.; Kiprof, P.; Riede, J.; Herrmann, W. A. *Organometallics* **1990**, *9*, 782. (e) Herrmann, W. A.; Roesky, P. W.; Scherer, W.; Kleine, M. *Organometallics* **1994**, *13*, 4536. (f) Jung, J.-H.; Hoffmann, D. M.; Lee, T. R. *J. Organomet. Chem.* **2000**, *599*, 112. (g) Papachristou, M.; Pirmettis, I. C.; Tsoukalas, C.; Papagiannopoulou, D.; Raptopoulou, C.; Terzis, A.; Stassinopoulou, C. I.; Chiotellis, E.; Pelecanou, M.; Papadopoulos, M. *Inorg. Chem.* **2003**, *42*, 5778. (h) Tzanopoulou, S.; Pirmettis, I. C.; Patsis, G.; Raptopoulou, C.; Terzis, A.; Papadopoulos, M.; Pelecanou, M. *Inorg. Chem.* **2006**, *45*, 902.

(30) (a) Shan, X.; Ellern, A.; Espenson, J. H. *Inorg. Chem.* **2002**, *41*, 7136. (b) Chattopadhyay, S.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem. Commun.* **2003**, *6*, 1358.

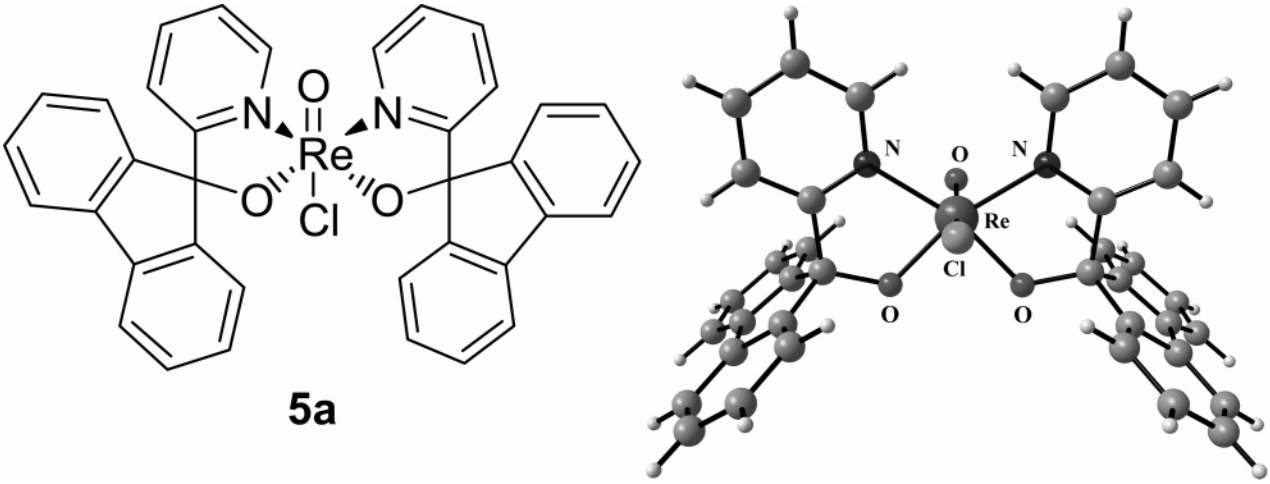


Figure 5. Bis(pyridylalkoxy)-substituted rhenium complex (**5a**) with a *trans*-oxo-chloro coordination (schematic view and a ball and stick[35,36] representation).

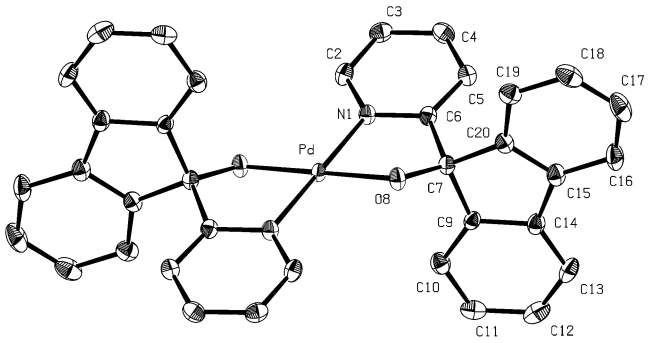


Figure 6. ORTEP style representation of the molecular structure of complex **6a** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity.

A main focus for the characterization of these new [ReOCl-$(L)_2$] complexes was the use of NMR spectroscopy combined with solid-state X-ray analysis. It was apparent from the ^{1}H NMR spectrum that complex **4a** was prepared in pure form, with only one structure type being present (Figure 4).

The N,O-ligands in this [ReOCl$(L)_2$] complex (**4a**) are inequivalent, according to the ^{1}H NMR spectrum, and therefore the structure type A can be excluded. In the ^{1}H NMR spectrum the H6′-signals of both pyridine rings are shifted downfield to 8.97 and 8.69 ppm and we expected that the pyridine rings are coordinated trans to electron withdrawing groups in this complex. Full characterization and classification was possible via H,H-DQF-COSY and a H,C-HSQC NMR-correlation (Table 2), but we were still not able to confidently determine the connectivity for this complex. The topology (type F) of **4a** was finally confirmed by single-crystal X-ray analysis (Figure 4). Crystal data and details of the structure determination are summarized in Table 4.

In the single-crystal X-ray structure the same structural motif as in complex **2a** was observed, where one of the ligands is coordinated with the alkoxide atom trans to the rhenyloxo fragment. The structural data for complex **4a** show no striking differences when compared to known Schiff base complexes. The second ligand is coordinated such that the pyridine ring is positioned trans to the chloro ligand.[31]

During the preparation of complex **4a**, we were also able to obtain the trans chloro-oxo rhenium complex **5a**, starting with complex **2a** (Figure 5). This trans chloro-oxo conformation makes complex **5a** a very rare example of type A complexes (Figure 3). To the best of our knowledge there are only four other rhenium(V) complexes known with a *trans*-[ReOCl$(L)_2$]-formula: [ReOCl(*o*-$C_6O_2Cl_4$)($Ph_2PCH_2CH_2PPh_2$)] {Re−O, 1.681 Å; Re−Cl, 2.467 Å; O−Re−Cl, 167.0°},[32] [ReOCl(NH_2CH_2-$CH_2S)_2$] {Re−O, 1.686 Å; Re−Cl, 2.596 Å; O−Re−Cl, 161.4°},[33] [ReOCl(NH(*o*-C_6H_4)$SCH_3)_2$] {Re−O, 1.711 Å; Re−Cl, 2.473 Å; O−Re−Cl, 158.3°},[34] and [ReOCl(OPhsal)-($P(CH_3)_2$Ph)] {Re−O, 1.652 Å; Re−Cl, 2.528 Å; O−Re−Cl, 171.7°}.[31a] The Re−O [1.6846(1) Å] and Re−Cl [2.4911(2) Å] bond lengths and the O−Re−Cl angle (159.0°) in complex **5a** are in agreement with the mentioned literature.

Palladium(II) and Copper(II) Complexes. The following section describes the synthesis of pyridinylalcoholate complexes of metals which are not typically utilized in epoxidation reactions. In terms of oxidation catalysis, palladium is of importance only as a catalyst in the Wacker-Process for the production of acetaldehyde, thus pyridinylalcoholate complexes of Pd are not expected to be useful catalysts.[37] The main interest was the coordination chemistry of these transition metals, especially of copper and palladium. Therefore we wanted to synthesize the corresponding Pd(II)-complexes of pyridyl alcohols. A better understanding of these complexes should build the basis of further catalytic experiments. The synthesis of these palladium and copper complexes was carried out according to a procedure first published by Shindo et. al in the 1960s.[17] Starting from the metal(II)−acetate complexes the two acetate ligands can be substituted with 2 equiv of the respective alkyl- or aryl-pyridyl alcohols (**a**−**d**, **f**, **g**) in this procedure, to form

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(35) Brandenburg K. *Diamond*, version 3.1d; Crystal Impact GbR: Bonn, Germany, 2006.

(36) Crystal structure analysis of compound **5a**: $C_{52}H_{60}ClN_3O_7Re_2$, M_r = 1246.90, green fragment (0.12 × 0.24 × 0.28 mm^3), orthorhombic, *Pnma* (No. 62), a = 20.467(3), b = 14.747(5), c = 17.514(1) Å, V = 5286(2) Å^3, Z = 4, d_{calcd} = 1.567 g cm^{-3}, F_{000} = 2464, μ = 4.676 mm^{-1}. A severe disorder of the target molecule forced us to abort any further refinement.

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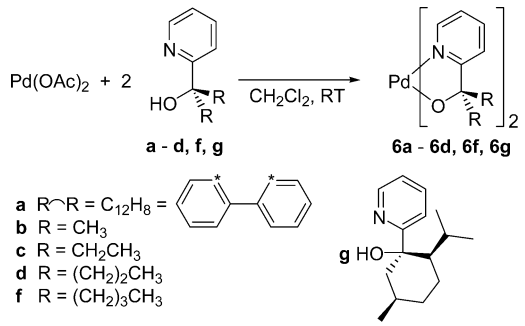
Table 4. Crystallographic Data for 2a, 4a·CH_2Cl_2, 6a, and 8a·2(CH_3OH)

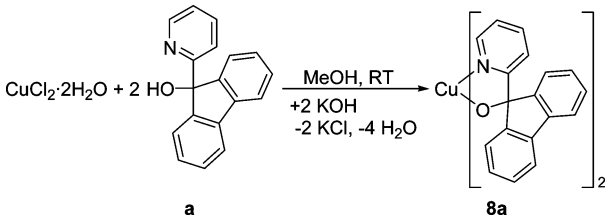
	2a	**4a**·CH_2Cl_2	**6a**	**8a**·2(CH_3OH)
formula	$C_{34}H_{48}Cl_3N_2O_2Re$	$C_{37}H_{26}Cl_3N_2O_3Re$	$C_{36}H_{24}N_2O_2Pd$	$C_{38}H_{32}CuN_2O_4$
fw	809.30	839.16	622.99	644.21
color/habit	dark green/plate	green/prism	yellow/plate	purple/needle
cryst size (mm^3)	0.05 × 0.33 × 0.41	0.20 × 0.28 × 0.51	0.11 × 0.25 × 0.25	0.25 × 0.25 × 0.64
cryst syst	triclinic	orthorhombic	monoclinic	trigonal
space group	$P\bar{1}$ (No. 2)	*Pbcn* (No. 60)	$P2_1/n$ (No. 14)	$R\bar{3}$ (No. 148)
a, Å	10.2270(8)	20.1010(8)	8.5458(12)	28.844(2)
b, Å	10.8980(8)	14.7122(5)	9.0653(4)	28.844(2)
c, Å	17.4706(18)	21.9827(10)	17.169(2)	9.304(1)
α, deg	72.465(8)	90	90	90
β, deg	81.166(8)	90	91.309(7)	90
γ, deg	68.837(6)	90	90	120
V, $Å^3$	1729.3(3)	6500.9(5)	1329.7(2)	6703.7(10)
Z	2	8	2	9
T, K	223	193	163	163
D_{calcd}, g cm^{-3}	1.554	1.715	1.556	1.436
μ, mm^{-1}	3.777	4.026	5.927	1.406
F(000)	816	3296	632	3015
θ range, deg	2.41 − 25.47	1.95 − 25.65	5.15 − 69.89	3.06 − 68.03
index ranges (*h*, *k*, *l*)	±12, ±13, ±21	±24, ±17, ±26	−10−0, −11−0, ±20	±34, ±34, −11−0
no. of reflns collected	22286	28378	2588	8685
no. of independent reflns/R_{int}	5939/0.083	6115/0.046	2413/0.024	2723/0.057
no. of obsd reflns ($I > 2\sigma(I)$)	5577	4781	2200	2468
no. of data/restraints/params	5939/0/403	6115/0 /417	2413/0 /188	2723/0 /270
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0372/0.0970	0.0270/0.0688	0.0374/0.1018	0.0367/0.0961
R1/wR2 (all data)[a]	0.0408/0.0988	0.0377/0.0711	0.0411/0.1044	0.0415/0.0995
GOF (on F^2)[a]	1.090	1.017	1.123	1.088
largest diff peak and hole (e $Å^{-3}$)	+1.93/−1.76	+1.50/−1.14	+1.38/−2.33	+0.35/−1.09

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Scheme 3. Preparation of the Palladium Complexes 6a−d, 6f, and 6g



Scheme 4. Preparation of the Copper Complex 8a



stable five-membered ring chelate adducts (**6a**−**d**, **6f**, **6g**). The complexes **6a**−**d**, **6f**, and **6g** precipitate from the reaction mixture and are further purified in very high yields by recrystallization (Scheme 3).

These complexes were characterized by ^1H- and ^{13}C NMR spectra. We recognized for the palladium and copper complexes that, in contrast to the rhenium complexes, the H6′ proton of the pyridine ring ligand cannot be used as a probe to follow the complexation rate. A possible reason for this is probably the trans coordination of the pyridine rings, which eliminates the effect obtained for the rhenium complexes. We found on the other hand that the C2′ and the quaternary carbon of the ligand can act now as an ideal probe for monitoring the complexation. The C2′ signal is shifted approximately 8 ppm to lower field to near the 170 ppm region, whereas the quaternary carbon of the ligand is also shifted around 15 ppm to lower field, compared to the free ligand. This effect can be explained by a shift of electron density toward the palladium atom. An X-ray structure of complex **6a** shows the expected square planar structure, where the oxygen atoms are mutually trans (Figure 6).[38] A selection of characteristic bond angles and bond distances are given in Table 3. Crystal data and details of the structure determination are presented in Table 4. The fluorenyl groups are coordinated perpendicular to the N_2O_2-plane containing the metal center. In comparison to other palladium complexes with N,O-ligands, for example the bis(8-hydroxyquinolinato)palladium(II) complex (**7**), no unusual complexation behavior was observed for complex **6a**. The Pd−O and Pd−N bond distances and the O−Pd−N angle in complex **6a** are very similar to complex (**7**) [Pd−O, 1.997−2.016 Å; Pd−N, 2.005−2.017 Å; O−Pd−N, 84.15−84.31°].[39]

We tried to prepare also the analogous distorted square planar copper(II) complex (**8a**). This copper(II) complex can be prepared according to the same procedure as the palladium complexes (**6**), starting with a copper(II) chloride precursor (Scheme 4).[40] A base for the deprotonation of the ligand is necessary in this synthetic protocol, because the chloride ion is, unsurprisingly, not basic enough to act as an internal base. Accordingly the ligand is dissolved in methanol and deprotonated with potassium hydroxide. Afterward the metal chloro-

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(39) Bond distances and angles were taken from the CCDC-database (V. 1.9; May 2007). (a) Kamenar, B.; Prout, C. K.; Wright, J. D. *J. Chem. Soc.* **1966**, 661. (b) Prout, C. K.; Wheeler, A. G. *J. Chem. Soc.* **1966**, 1286.

(40) Kunze, U. R.; Schwecht, G. *Grundlagen der Quantitativen und Qualitativen Analyse (Basics of Quantitative and Qualitative Analysis)*, 4th ed.; Thieme: Stuttgart, Germany, 1996.

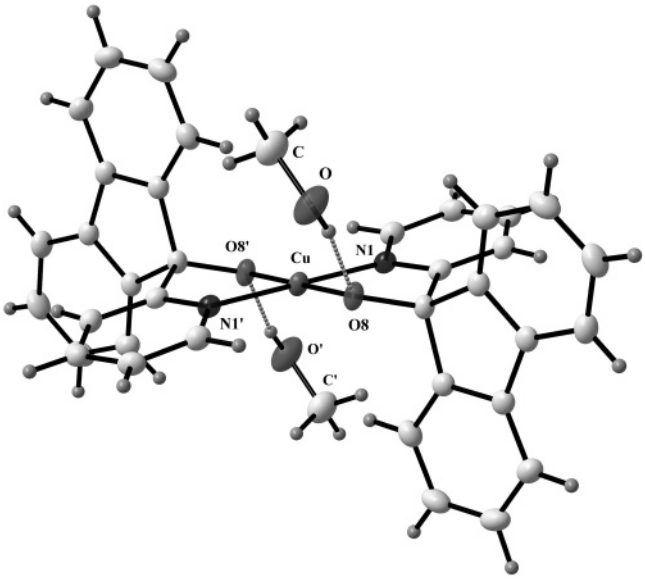

Figure 7. ORTEP style representation[35] of the molecular structure of complex **8a** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity.

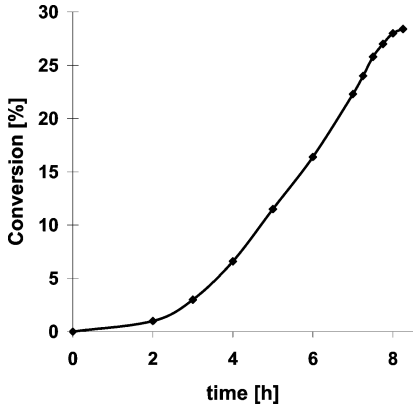

Figure 8. Epoxidation of cyclooctene using catalyst **4a**.

hydrate[41] was added, and after a few minutes a purple precipitate was obtained. Suitable crystals for single-crystal X-ray studies were obtained by recrystallization from a methanol/*n*-hexane solution (Figure 7). A selection of characteristic bond angles and bond distances for complex **8a** are given in Table 3. Crystal data and details of the structure determination are presented in Table 4. In the solid-state structure two molecules of methanol are cocrystallized in the unit cell, which are coordinated via a hydrogen bridge to the oxygen O8 of the ligand [$CH_3OH\cdots O$, 1.93(4); $O(H)\cdots O$ 2.771(3); $\angle O-H\cdots O$, 172(3)°]. Therefore the copper is pseudo-octahedrally coordinated by two methanol molecules [$Cu\cdots O(H)$, 3.193(7); $Cu\cdots H(O)$, 3.21(5)].

Catalytic Results. Rhenium(V)-salen catalysts have shown good results in the past with the cyclooctene/TBHP epoxidation system.[31b,42] Accordingly, the newly prepared catalysts were tested with this model system. However, during testing we found that all [$ReOCl_3(L)$] type complexes (**3**) partially decomposed during the reaction. A decolorization occurs from the typically greenish rhenium(V) species after a few minutes, providing the colorless perrhenate ion and free ligand. Application of **3** to the hydrogen peroxide/cyclooctene catalytic system also failed.

In contrast to the monosubstituted compounds [$ReOCl_3(L)$]-(NBu_4) (**3**), the rhenium(V) complexes [$ReOCl(L)_2$] (**4**) are stable under catalytic conditions. A significant catalytic activity was obtained with these systems for the formation of cyclooctene oxide during the first 8 h, and an example using catalyst **4a** is shown in Figure 8. The nature of the solvent (chloroform or *n*-decane), in which the TBHP is dissolved, does not appear to influence the catalytic activity. A surprising point was that the reaction can be restarted by reheating after cooling the reaction mixture. The catalytic activity is constant and the catalytically active species does not appreciably decompose.

Using complexes **6** and **8** we tried the same reaction conditions as for the catalysts **3** and **4**, but we could not obtain any epoxidation products.

Conclusion

A comprehensive series of complexes of pyridylalcoholate ligands of Re, Pd, and Cu was prepared and isolated using reliable and simple synthetic methods. Of note, a rare example of a trans chloro-oxo rhenium complex was selectively prepared by careful adjustment of experimental conditions. The connectivity of the complexes was reliably deduced by single-crystal X-ray crystallography or by the comparison of NMR data of structurally characterized complexes with the remaining complexes. All complexes were tested as catalysts in epoxidation reactions, and the [$ReOCl(L)_2$] type complexes were found to be a promising family of robust and synthetically convenient precatalysts.

Experimental Section

General Considerations. The ligands **a**, **e**,[43] **b**−**d**, **f**,[8] and **g**[44] were prepared according to the literature. The lithium pyridinyl alcoholates (**a***, **b***) were prepared according to literature methods.[7,43,45] All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried over activated molecular sieves and refluxed over appropriate drying agents under argon. ^1H and ^{13}C NMR spectra were recorded on a JEOL-JMX-GX 270 or 400 MHz spectrometer at room temperature and referenced to the residual ^1H and ^{13}C signals of the solvents. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet. Coupling constants *J* are given in Hz. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 (EI) or a Varian MAT 311a (CI) instrument. IR spectra were recorded on a Perkin-Elmer 1650 FT-IR spectrophotometer using KBr discs.

Tetrabutylammonium-*trans*{[*N*,*O*-(9-(2′-pyridyl)fluoren-9-olato)]trichlorooxorhenate(V)} (2a). At −40 °C 0.7 mmol of the lithium precursor (**a***) was added to a solution of 400 mg (0.7 mmol) tetrabutylammonium tetrachlorooxorhenate(V) [$ReOCl_4$](NBu_4) (**1**) dissolved in 30 mL of THF (EtOH). The solution was heated slowly to room temperature, whereby the color changed from yellow to dark green. After 30 min under vigorous stirring the solvent was reduced in vacuo to one-third to precipitate the green product. The colorless THF was removed via syringe, and the solid was washed twice with 10 mL of cold THF and afterward dried in vacuo. Yield: 0.46 g (82%). ^1H NMR (400 MHz, d_6-DMSO): δ = 8.18

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(1H, d, $^3J_{H6',H5'}$ = 5 Hz, H6′), 7.89 (2H, d, $^3J_{H1/5,H2/6}$ = 9 Hz, H1,5), 7.79 (2H, d, H4,8), 7.59 (1H, dd, $^3J_{H4',H3'}$ = 8 Hz, $^3J_{H4',H5'}$ = 8 Hz, H4′), 7.36 (2H, dd, $^3J_{H3/7,H4/8}$ = 8 Hz, $^3J_{H3/7,H2/6}$ = 8 Hz, H3,7), 7.16 (2H, dd, H2,6), 7.32 (1H, dd, $^3J_{H5',H6'}$ = 6 Hz, $^3J_{H5',H4'}$ = 7 Hz, H5′), 6.57 (1H, d, $^3J_{H3',H4'}$ = 8 Hz, H3′), 3.15 (8H, t, NCH_2), 1.54 (8H, m, NCH_2CH_2), 1.30 (8H, m, $NCH_2CH_2CH_2$), 0.89 (12H, t, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, d_6-DMSO): δ = 166.1 (C2′), 148.2 (C6′), 147.2 (C10,11), 143.8 (C12,13), 139.5 (C4′), 129.4 (C1,5), 127.8 (C3,7), 122.4 (C2,6), 119.8 (C3′), 119.8 (C5′), 119.4 (C4,8), 96.6 (*C*O), 57.5 (NCH_2), 23.0 (NCH_2CH_2), 19.1 ($NCH_2CH_2CH_2$), 13.4 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{34}H_{48}Cl_3N_2O_2Re$ (809.30): C, 50.46; H, 5.98; N, 3.46; Cl, 13.14. Found: C, 50.42; H, 5.97; N, 3.22; Cl, 12.15%. IR (KBr, cm^{-1}): ν = 956 (Re═O, s).

Preparation of Complexes 3a−e via the Free Ligand Method. At −40 °C 1.4 mmol of the pyridyl ligand (**a**−**e**) was added to a solution of 400 mg (0.7 mmol) of tetrabutylammonium tetrachlorooxorhenate(V) [$ReOCl_4$](NBu_4) (**1**) dissolved in 30 mL of THF (EtOH). The solution was heated slowly to room temperature, whereby the color changed from yellow to dark green. After 30 min under vigorous stirring the solvent was reduced in vacuo to one-third to precipitate the green product. The colorless THF was removed via syringe, and the solid was washed twice with 10 mL of cold THF and afterward dried in vacuo.

Tetrabutylammonium-*cis*{[*N*,*O*-(9-(2′-pyridyl)fluoren-9-olato)]trichlorooxorhenate(V)} (3a). Yield: 0.41 g (72%). ^1H NMR (400 MHz, d_6-DMSO): δ = 9.12 (1H, d, $^3J_{H6',H5'}$ = 5 Hz, H6′), 8.62 (1H, dd, $^3J_{H4',H3'}$ = 8 Hz, $^3J_{H4',H5'}$ = 8 Hz, H4′), 8.28 (2H, d, $^3J_{H1/5,H2/6}$ = 9 Hz, H1,5), 8.24 (1H, dd, $^3J_{H5',H6'}$ = 6 Hz, $^3J_{H5',H4'}$ = 7 Hz, H5′), 7.85 (2H, dd, $^3J_{H3/7,H4/8}$ = 8 Hz, $^3J_{H3/7,H2/6}$ = 8 Hz, H3,7), 7.76 (2H, d, H2,6), 7.70 (2H, dd, H4,8), 7.58 (1H, d, $^3J_{H3',H4'}$ = 8 Hz, H3′), 3.15 (8H, t, NCH_2), 1.54 (8H, m, NCH_2CH_2), 1.30 (8H, m, $NCH_2CH_2CH_2$), 0.89 (12H, t, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, d_6-DMSO): δ = 166.9 (C2′), 149.2 (C6′), 147.0 (C10,11), 140.1 (C12,13), 136.9 (C4′), 128.2 (C1,5), 128.0 (C3,7), 124.3 (C2,6), 122.4 (C3′), 120.0 (C5′), 119.8 (C4,8), 82.4 (*C*O), 59.5 (NCH_2), 24.3 (NCH_2CH_2), 19.8 ($NCH_2CH_2CH_2$), 13.8 ($NCH_2CH_2CH_2CH_3$).

Tetrabutylammonium{[*N*,*O*-(2-(2′-pyridyl)propan-2-olato)]trichlorooxorhenate(V)} (3b). Yield: 0.36 g (76%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.18 (1H, d, $^3J_{H6',H5'}$ = 5 Hz, H6′), 7.32 (1H, dd, $^3J_{H4',H3'}$ = 8 Hz, $^3J_{H4',H5'}$ = 8 Hz, H4′), 7.31 (1H, d, $^3J_{H3',H4'}$ = 8 Hz, H3′), 7.21 (1H, t, $^3J_{H5',H6'}$ = 5 Hz, $^3J_{H5',H4'}$ = 8 Hz, H5′), 3.25 (8H, t, NCH_2), 1.62 (8H, m, NCH_2CH_2), 1.53 (6H, s, $C(CH_3)_2$), 1.41 (8H, m, $NCH_2CH_2CH_2$), 0.95 (12H, t, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ = 170.1 (C2′), 148.0 (C6′), 142.7 (C4′), 121.6 (C3′), 118.1 (C5′), 87.9 (*C*O), 59.1 (NCH_2), 29.1 ($C(CH_3)_2$), 24.1 (NCH_2CH_2), 19.7 ($NCH_2CH_2CH_2$), 13.7 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{24}H_{46}Cl_2N_2O_2Re$ (687.2): C, 41.95; H, 6.75; N, 4.08. Found: C, 41.45; H, 6.37; N, 3.82%.

Tetrabutylammonium{[*N*,*O*-(3-(2′-pyridyl)pentan-3-olato)]trichlorooxorhenate(V)} (3c). Yield: 0.31 g (66%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20 (1H, d, $^3J_{H6',H5'}$ = 4 Hz, H6′), 7.30 (1H, dd, $^3J_{H4',H3'}$ = 8 Hz, $^3J_{H4',H5'}$ = 8 Hz, H4′), 7.28 (1H, dd, $^3J_{H5',H6'}$ = 4 Hz, $^3J_{H5',H4'}$ = 8 Hz, H5′), 7.13 (1H, d, $^3J_{H3',H4'}$ = 8 Hz, H3′), 3.22 (8H, t, NCH_2), 1.85 (4H, m, $C(CH_2)_2$), 1.61 (8H, m, NCH_2CH_2), 1.38 (8H, m, $NCH_2CH_2CH_2$), 0.90 (12H, t, $NCH_2CH_2CH_2CH_3$), 0.75 (6H, t, $^3J_{HH}$ = 7 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ = 168.9 (C2′), 148.7 (C6′), 142.2 (C4′), 121.4 (C3′), 118.2 (C5′), 93.4 (*C*O), 58.9 (NCH_2), 31.8 ($C(CH_2)_2$), 24.1 (NCH_2CH_2), 19.7 ($NCH_2CH_2CH_2$), 13.7 ($NCH_2CH_2CH_2CH_3$), 8.9 (CH_3). Anal. Calcd for $C_{26}H_{50}Cl_2N_2O_2Re$ (715.25): C, 43.66; H, 7.05; N, 3.92. Found: C, 44.06; H, 7.03; N, 3.94%. IR (KBr, cm^{-1}): ν = 938 (Re═O, s).

Tetrabutylammonium{[*N*,*O*-(4-(2′-pyridyl)heptan-4-olato)]trichlorooxorhenate(V)} (3d). Yield: 0.37 g (72%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.25 (1H, d, $^3J_{H6',H5'}$ = 5 Hz, H6′), 7.33 (1H, dd, $^3J_{H4',H3'}$ = 8 Hz, $^3J_{H4',H5'}$ = 8 Hz, H4′), 7.29 (1H, dd, $^3J_{H5',H6'}$ = 4 Hz, $^3J_{H5',H4'}$ = 8 Hz, H5′), 7.18 (1H, d, $^3J_{H3',H4'}$ = 8 Hz, H3′), 3.30 (8H, t, NCH_2), 1.81 (4H, m, $C(CH_2)_2$), 1.63 (8H, m, NCH_2CH_2), 1.38 (8H, m, $NCH_2CH_2CH_2$), 1.41 (4H, m, CCH_2CH_2), 0.99 (12H, t, $NCH_2CH_2CH_2CH_3$), 0.78 (6H, t, $^3J_{HH}$ = 6 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ = 169.5 (C2′), 148.7 (C6′), 142.1 (C4′), 126.0 (C3′), 118.2 (C5′), 93.2 (*C*O), 59.5 (NCH_2), 42.0 ($C(CH_2)_2$), 24.3 (NCH_2CH_2), 19.8 ($NCH_2CH_2CH_2$), 17.6 (CCH_2CH_2), 14.5 ($CCH_2CH_2CH_3$), 13.8 ($NCH_2CH_2CH_2CH_3$).

Tetrabutylammonium{[*N*,*O*-(1,1-diphenyl-1-(2′-pyridyl)methan-1-olato)]trichlorooxorhenate(V)} (3e). Yield: 0.25 g (45%). ^1H NMR (270 MHz, $CDCl_3$): δ = 8.26 (1H, d, $^3J_{H6',H5'}$ = 5 Hz, H6′), 7.55−7.18 (13H, m), 3.11 (8H, t, NCH_2), 1.52 (8H, m, NCH_2CH_2), 1.31 (8H, m, $NCH_2CH_2CH_2$), 0.88 (12H, t, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (67.8 MHz, $CDCl_3$): δ = 166.5 (C2′), 149.0 (C6′), 145.1 (C1″,1‴), 141.6 (C4′), 128.7 (C2″,2‴), 128.1 (C3″,3‴), 127.9 (C6″,6‴), 127.8 (C5″,5‴), 127.3 (C4″,4‴), 122.2 (C3′), 121.8 (C5′), 96.1 (*C*O), 59.8 (NCH_2), 24.4 (NCH_2CH_2), 19.9 ($NCH_2CH_2CH_2$), 13.8 ($NCH_2CH_2CH_2CH_3$).

Preparation of Complexes 4a and 4b. A 400 mg portion of tetrabutylammonium tetrachlororhenate(V) [$ReOCl_4$](NBu_4) (**1**) was dissolved in 20 mL of ethanol and cooled to −20 °C, and 2.8 mmol of the pyridyl ligand was added. The dark green solution was refluxed for 2 h. After 30 min a green precipitate occurs. After cooling to room temperature the solvent was removed via a drain tube, and the precipitate was washed twice with diethyl ether. The solid was dried in vacuo and recrystallized from a dichloromethane/diethyl ether solution.

Bis{*N*,*O*-[9-(2′-pyridyl)fluoren-9-olato]}chlorooxorhenium-(V) (4a). Yield: 0.41 g (79%). ^1H NMR (270 MHz, d_6-DMSO): δ = 8.97 (1H, d, $^3J_{H6',H5'}$ = 6 Hz, H6′), 8.69 (1H, d, $^3J_{H6'',H5''}$ = 5 Hz, H6″), 8.07 (1H, dd, $^3J_{H5'',H4''}$ = 7 Hz, $^3J_{H4'',H3''}$ = 8 Hz, H4″), 7.91 (1H, d, $^3J_{H6,H5}$ = 8 Hz, H6), 7.84 (5H, m, H6, H4′, H3‴, H6‴, H6‴), 7.82 (1H, dd, $^3J_{H6'',H5''}$ = 5 Hz, $^3J_{H5'',H4''}$ = 7 Hz, H5″), 7.53 (1H, dd, $^3J_{H6',H5'}$ = 8 Hz, $^3J_{H5',H4'}$ = 8 Hz, H5′), 7.44 (1H, dd, $^3J_{H5,H4}$ = 8 Hz, $^3J_{H4,H3}$ = 8 Hz, H4), 7.37 (1H, dd, $^3J_{H6''',H5'''}$ = 8 Hz, $^3J_{H5''',H4'''}$ = 8 Hz, H5‴), 7.31 (1H, dd, $^3J_{H5,H4}$ = 8 Hz, $^3J_{H4,H3}$ = 8 Hz, H4), 7.26 (1H, dd, $^3J_{H5''',H4'''}$ = 8 Hz, $^3J_{H4''',H3'''}$ = 8 Hz, H4‴), 7.24 (1H, dd, $^3J_{H6,H5}$ = 8 Hz, $^3J_{H5,H4}$ = 8 Hz, H5), 7.19 (1H, dd, $^3J_{H5''',H4'''}$ = 8 Hz, $^3J_{H4''',H3'''}$ = 8 Hz, H4‴), 7.09 (1H, d, $^3J_{H4'',H3''}$ = 8 Hz, H3″), 6.99 (1H, d, $^3J_{H4,H3}$ = 8 Hz, H3), 6.88 (1H, d, $^3J_{H4''',H3'''}$ = 8 Hz, H3‴), 6.86 (1H, dd, $^3J_{H6,H5}$ = 7 Hz, $^3J_{H5,H4}$ = 8 Hz, H5), 6.70 (1H, d, $^3J_{H4',H3'}$ = 8 Hz, H3′), 6.66 (1H, dd, $^3J_{H6''',H5'''}$ = 8 Hz, $^3J_{H5''',H4'''}$ = 8 Hz, H5‴), 6.18 (1H, d, $^3J_{H4,H3}$ = 8 Hz, H3). $^{13}C\{^1H\}$ NMR (67.8 MHz, d_6-DMSO): δ = 169.5 (C2′), 166.2 (C2′), 154.2 (C6′), 150.5 (C6′), 149.1 (C10,11), 148.3 (C10,11), 148.1 (C10,11), 148.0 (C10,11), 143.8 (C4′), 143.2 (C4′), 139.9 (C12,13), 139.8 (C12,13), 139.3 (C12,13), 139.0 (C12,13), 129.7 (C1,5), 129.7 (C1,5), 129.5 (C1,5), 129.4 (C1,5), 128.7 (C3,7), 128.1 (C3,7), 127.9 (C3,7), 127.8 (C3,7), 127.0 (C2,6), 126.9 (C2,6), 125.8 (C2,6), 125.4 (C2,6), 124.2 (C3′), 124.0 (C3′), 123.1 (C5′), 121.9 (C5′), 120.6 (C4,8), 120.4 (C4,8), 120.4 (C4,8), 120.1 (C4,8), 114.5 (*C*O), 95.0 (*C*O). IR (KBr, cm^{-1}): ν = 941 (Re═O, s).

Bis{*N*,*O*-[2-(2′-pyridyl)propan-2-olato]}chlorooxorhenium-(V) (4b). Yield: 0.29 g (81%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.79 (1H, d, ^3J = 5 Hz), 8.69 (1H, d, ^3J = 5 Hz), 8.07 (1H, dd, $^3J_{H4,H3}$ = 8 Hz, $^3J_{H4,H5}$ = 8 Hz, H4), 7.84 (1H, m), 7.82 (1H, dd, $^3J_{H5,H6}$ = 5 Hz, $^3J_{H5,H4}$ = 8 Hz, H5), 7.53 (1H, dd, $^3J_{H5,H6}$ = 8 Hz, $^3J_{H5,H4}$ = 8 Hz, H5), 7.09 (1H, d, ^3J = 8 Hz), 6.70 (1H, d, ^3J = 8 Hz), 1.56 (6H, s, $C(CH_3)_2$), 1.52 (6H, s, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ = 172.8 (C2), 169.6 (C2), 152.5 (C6), 147.4 (C6), 142.2 (C4), 141.9 (C4), 124.3 (C3), 122.1 (C3), 119.4 (C5), 118.4 (C5), 103.3 (*C*O), 84.4 (*C*O), 30.4 ($C(CH_3)_2$), 29.0 ($C(CH_3)_2$), 28.6 ($C(CH_3)_2$), 28.0 ($C(CH_3)_2$). IR (KBr, cm^{-1}): ν = 941 (Re═O, s).

Preparation of Complexes 6a−g. To a solution of 2.2 mmol palladium acetate dissolved in 20 mL of dichloromethane, 4.4 mmol of the pyridyl ligand (**a**−**d**, **f**, **g**) was added with vigorous stirring.

During the first 30 min the dark orange solution lightened to yellow. The solvent was reduced in vacuo to 10 mL, and 10 mL of diethyl ether was added, whereupon the product precipitated as yellow crystals. After filtration to remove the formed acetic acid, the precipitate was washed with 10 mL of diethyl ether, and the product was dried in vacuo.

Bis{*N,O*-[9-(2′-pyridyl)fluoren-9-olato]}palladium(II) (6a). Yield: 1.11 g (81%). ^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 8.35 (1H, d, $^3J_{H6',H5'}$ = 5 Hz, H$^{6'}$), 8.27 (2H, d, $^3J_{H1/5,H2/6}$ = 9 Hz, H^{1,5}), 7.45 (1H, dd, $^3J_{H4',H3'}$ = 8 Hz, $^3J_{H4',H5'}$ = 8 Hz, H$^{4'}$), 7.70 (2H, dd, $^3J_{H3/7,H4/8}$ = 8 Hz, $^3J_{H3/7,H2/6}$ = 8 Hz, H^{3,7}), 7.40 (4H, m, H^{2,4,6,8}), 7.06 (1H, dd, $^3J_{H5',H6'}$ = 5 Hz, $^3J_{H5',H4'}$ = 7 Hz, H$^{5'}$), 6.49 (1H, d, $^3J_{H3',H4'}$ = 8 Hz, H$^{3'}$). ^{13}C{^{1}H} NMR (100.5 MHz, 300 K, $CDCl_3$): δ = 173.5 (C$^{2'}$), 150.4 (C$^{6'}$), 149.1 (C^{10,11}), 139.7 (C^{12,13}), 138.4 (C$^{4'}$), 129.0 (C^{1,5}), 128.4 (C^{3,7}), 125.3 (C^{2,6}), 122.7 (C$^{3'}$), 121.4 (C$^{5'}$), 120.0 (C^{4,8}), 94.1 (C^9). Anal. Calcd for $C_{36}H_{24}N_2O_2Pd$ (622.99): C, 69.40; H, 3.88; N, 4.50. Found: C, 69.5; H, 3.8; N, 4.3%.

Bis{*N,O*-[2-(2′-pyridyl)propan-2-olato]}palladium(II) (6b). Yield: 0.72 g (86%). ^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 8.49 (1H, d, $^3J_{H6',H5'}$ = 5 Hz, H$^{6'}$), 7.78 (1H, dd, $^3J_{H4',H3'}$ = 8 Hz, $^3J_{H4',H5'}$ = 8 Hz, H$^{4'}$), 7.22 (1H, d, $^3J_{H3',H4'}$ = 8 Hz, H$^{3'}$), 7.11 (1H, t, $^3J_{H5',H6'}$ = 5 Hz, $^3J_{H5',H4'}$ = 8 Hz, H$^{5'}$), 1.60 (6H, s, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, 300 K, $CDCl_3$): δ = 170.1 (C$^{2'}$), 148.0 (C$^{6'}$), 142.7 (C$^{4'}$), 121.6 (C$^{3'}$), 118.1 (C$^{5'}$), 87.9 (*C*O), 30.6 (*C*H$_3$). Anal. Calcd for $C_{16}H_{22}N_2O_2Pd$ (380.78): C, 50.47; H, 5.82; N, 7.36. Found: C, 50.03; H, 5.70; N, 6.64%.

Bis{*N,O*-[3-(2′-pyridyl)pentan-3-olato]}palladium(II) (6c). Yield: 0.64 g (67%). ^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 8.42 (1H, d, $^3J_{H6',H5'}$ = 4 Hz, H$^{6'}$), 7.60 (1H, dd, $^3J_{H4',H3'}$ = 8 Hz, $^3J_{H4',H5'}$ = 8 Hz, H$^{4'}$), 7.18 (1H, d, $^3J_{H3',H4'}$ = 8 Hz, H$^{3'}$), 7.08 (1H, dd, $^3J_{H5',H6'}$ = 4 Hz, $^3J_{H5',H4'}$ = 8 Hz, H$^{5'}$), 1.78 (2H, m, C*H*$_2$), 1.70 (2H, m, C*H*$_2$), 0.59 (6H, t, $^3J_{HH}$ = 7 Hz, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, 300 K, $CDCl_3$): δ = 167.2 (C$^{2'}$), 146.9 (C$^{6'}$), 136.6 (C$^{4'}$), 121.4 (C$^{3'}$), 119.4 (C$^{5'}$), 76.2 (*C*O), 34.5 (*C*H$_2$), 7.5 (*C*H$_3$).

Bis{*N,O*-[4-(2′-pyridyl)heptan-4-olato]}palladium(II) (6d). Yield: 0.76 g (63%). ^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 8.42 (1H, d, $^3J_{H6',H5'}$ = 5 Hz, H$^{6'}$), 7.67 (1H, dd, $^3J_{H4',H3'}$ = 7 Hz, $^3J_{H4',H5'}$ = 7 Hz, H$^{4'}$), 7.25 (1H, d, $^3J_{H3',H4'}$ = 8 Hz, H$^{3'}$), 7.08 (1H, dd, $^3J_{H5',H6'}$ = 6 Hz, $^3J_{H5',H4'}$ = 5 Hz, H$^{5'}$), 1.78 (2H, m, C*H*$_2$), 1.68 (2H, m, C*H*$_2$), 1.14 (2H, m, C*H*$_2$), 0.80 (2H, m, C*H*$_2$), 0.79 (6H, t, $^3J_{HH}$ = 6 Hz, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, 300 K, $CDCl_3$): δ = 174.4 (C$^{2'}$), 148.8 (C$^{6'}$), 137.5 (C$^{4'}$), 122.0 (C$^{3'}$), 121.4 (C$^{5'}$), 86.9 (*C*O), 45.5 (*C*H$_2$), 17.2 (*C*H$_2$), 14.7 (*C*H$_3$).

Bis{*N,O*-[5-(2′-pyridyl)nonan-5-olato]}palladium(II) (6f). Yield: 0.68 g (54%). ^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 8.45 (1H, d, $^3J_{H6',H5'}$ = 5 Hz, H$^{6'}$), 7.72 (1H, dd, $^3J_{H4',H3'}$ = 7 Hz, $^3J_{H4',H5'}$ = 6 Hz, H$^{4'}$), 7.16 (1H, d, $^3J_{H3',H4'}$ = 8 Hz, H$^{3'}$), 6.97 (1H, dd, $^3J_{H5',H6'}$ = 6 Hz, $^3J_{H5',H4'}$ = 6 Hz, H$^{5'}$), 1.74 (2H, m, C*H*$_2$), 1.58 (2H, m, C*H*$_2$), 1.25 (2H, m, C*H*$_2$), 1.09 (2H, m, C*H*$_2$), 0.81 (2H, m, C*H*$_2$), 0.80 (6H, t, $^3J_{HH}$ = 7 Hz, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, 300 K, $CDCl_3$): δ = 174.6 (C$^{2'}$), 149.1 (C$^{6'}$), 137.8 (C$^{4'}$), 122.3 (C$^{3'}$), 121.1 (C$^{5'}$), 87.3 (*C*O), 42.7 (CO*C*H$_2$), 26.1 (*C*H$_2$), 23.2 (*C*H$_2$), 14.0 (*C*H$_3$).

Bis{*N,O*-[(1*S*,2*S*,5*R*)-5-methyl-2-isopropyl-1-(2′-pyridyl)cyclohexan-1-olato]}palladium(II) (6g). Yield: 1.04 g (83%). ^{1}H NMR (400 MHz, 300 K, $CDCl_3$): δ = 8.37 (1H, d, $^3J_{H6',H5'}$ = 6 Hz, H$^{6'}$), 7.65 (1H, dd, $^3J_{H4',H3'}$ = 6 Hz, $^3J_{H4',H5'}$ = 8 Hz, H$^{4'}$), 7.12 (1H, t, $^3J_{H5',H6'}$ = 6 Hz, $^3J_{H5',H4'}$ = 8 Hz, H$^{5'}$), 7.00 (1H, d, $^3J_{H3',H4'}$ = 6 Hz, H$^{3'}$), 2.05 (1H, m, H^5), 1.90 (1H, ddd, $^3J_{H4eq,H5}$ = 2 Hz, $^3J_{H4eq,H4ax}$ = 12 Hz, $^3J_{H4eq,H3ax}$ = 2 Hz, H^{4eq}), 1.78 (1H, dddd, $^3J_{H3ax,H3eq}$ = 12 Hz, $^3J_{H3ax,H2}$ = 12 Hz, $^3J_{H3ax,H4ax}$ = 12 Hz, $^3J_{H3ax,H4eq}$ = 4 Hz, H^{3ax}), 1.70 (1H, dd, $^3J_{H2,H3eq}$ = 4 Hz, $^3J_{H2,H3ax}$ = 12 Hz, H^2), 1.48 (1H, dddd, $^3J_{H3eq,H3ax}$ = 12 Hz, $^3J_{H3eq,H4eq}$ = 2 Hz, $^3J_{H3eq,H4ax}$ = 4 Hz, $^3J_{H3eq,H2}$ = 2 Hz, H^{3eq}), 1.22 (1H, ddd, $^3J_{H6eq,H6ax}$ = 12.5 Hz, $^3J_{H6eq,H5}$ = 2 Hz, $^4J_{H6eq,H4eq}$ = 2 Hz, H^{6eq}), 1.18 (1H, dd, $^3J_{H6ax,H6eq}$ = 12.5 Hz, $^3J_{H6ax,H5}$ = 12.5 Hz, H^{6ax}), 1.10 (3H, d, $^3J_{H(CH3),H5}$ = 6.5 Hz, C*H*$_3$), 0.91 (1H, sept., $^3J_{H(CH),H(CH3)2}$ = 7 Hz, C*H*(CH$_3$)$_2$), 0.89 (1H, dddd, $^3J_{H4ax,H4eq}$ = 12.5 Hz, $^3J_{H4ax,H5}$ = 12.5 Hz, $^3J_{H4ax,H3ax}$ = 12.5 Hz, $^3J_{H4ax,H3eq}$ = 4 Hz, H^{4ax}), 0.81 (3H, d, $^3J_{H(CH3),CH}$ = 7 Hz, C*H*$_3$), 0.60 (3H, d, $^3J_{H(CH3),CH}$ = 6.5 Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (100.5 MHz, 300 K, $CDCl_3$): δ = 180.5 (C$^{2'}$), 147.5 (C$^{6'}$), 137.1 (C$^{4'}$), 121.5 (C$^{3'}$), 121.3 (C$^{5'}$), 87.9 (C^1), 52.8 (C^6), 51.4 (C^2, d, $^1J_{CH}$ = 127 Hz), 35.7 (*C*H(CH$_3$)$_2$), 27.8 (C^5), 27.7 ((CH$_2$)$_2$-CH*C*H$_3$), 24.1 (C^4), 22.5 (*C*H$_3$), 21.9 (C^3), 18.5 (*C*H$_3$).

Bis{*N,O*-[9-(2′-pyridyl)fluoren-9-olato]}copper(II) (8a). In 50 mL of dry methanol 0.7 g (12.5 mmol) of KOH was completely dissolved. A clear solution was observed after addition of 1.5 g (6.0 mmol) of ligand **a** (9-(2-pyridyl)-9-fluorenol) to the KOH solution. After 10 min 0.5 g (3.0 mmol) of $CuCl_2 \cdot 2H_2O$ was added, the color changed to violet, and a voluminous violet precipitate emerged. After 20 min the precipitate was left to settle, and the methanol supernatant was removed via syringe. The precipitate was washed three times with 10 mL of methanol and dried in vacuo. The product was purified by crystallization from a CH_2Cl_2/*n*-hexane solution to obtain purple needles. Yield: 1.32 g (76%). Anal. Calcd for $C_{36}H_{24}N_2O_2Cu \cdot 2(CH_3OH)$ (644.21): C, 70.85; H, 5.01; N, 4.35; Cu, 9.86. Found: C, 70.7; H, 4.9; N, 4.1; Cu, 10.1%. IR (KBr, cm^{-1}): ν = 497 (Cu−O), 421.

Procedure for the Epoxidation of Cyclooctene with *tert*-Butylhydrogenperoxide. In a Schlenk tube equipped with a stirring bar cyclooctene (50 mmol), 50 μL of dibutyl ether as internal standard, and 50 μmol catalyst were added. After warming to a steady 50 °C a *tert*-butyl hydrogenperoxide/*n*-decane solution (50 mmol) was added. Every 30 min a sample was analyzed by gas chromatography.

Single-Crystal X-ray Structure Determination of Compounds 2a, 4a·CH$_2$Cl$_2$, 6a, and 8a·2(CH$_3$OH). **General**. Crystal data and details of the structure determination are presented in Table 4. Suitable single-crystals for the X-ray diffraction studies were grown with standard cooling techniques. Crystals were stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out either on an area detecting system and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) or an automated four-circle diffractometer and graphite-monochromated Cu Kα radiation (λ = 1.54180 Å). The unit cell parameters were obtained by full-matrix least-squares refinements. Data collections were performed at low temperatures (either Oxford Cryosystems cooling device or Nonius cooling device). Intensities were integrated, and the raw data were corrected for Lorentz and polarization effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL 97 weighting scheme and stopped at shift/err <0.002. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography. All calculations were performed with the WinGX system, including the programs PLATON, SHELXL 97, and SIR 92.[35,46]

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Specials. 2a: (IPDS, Stoe&Cie; rotating anode, Nonius FR591; one data set in oscillation scan modus with $\Delta\varphi = 1.00°$ and dx = 70 mm; $T = 223$ K; corrections for absorption and decay were applied). Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{C-H} = 0.97$ Å and $U_{iso(H)} = 1.5U_{eq(C)}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and aromatic d_{C-H} distances of 0.98 and 0.94 Å, respectively, and $U_{iso(H)} = 1.2U_{eq(C)}$. A disorder [58(2):42(2)] in one branch of the tetrabutylammonium cation could be resolved clearly. **4a·(CH_2Cl_2)**: (IPDS, Stoe&Cie; rotating anode, Nonius FR591; one data set in oscillation scan modus with $\Delta\varphi = 1.00°$ and dx = 70 mm; $T = 193$ K; corrections for absorption and decay were applied). All hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and aromatic d_{C-H} distances of 0.99 and 0.95 Å, respectively, and $U_{iso(H)} = 1.2U_{eq(C)}$. Small extinction effects were corrected with the SHELXL 97 procedure [$\epsilon = 0.00033(5)$]. **6a**: (Nonius, CAD4; sealed tube, Nonius FR590; $T = 163$ K; correction for absorption was applied). Small extinction effects were corrected with the SHELXL 97 procedure [$\epsilon = 0.0036(4)$]. All hydrogen atoms were placed in ideal positions and refined using a riding model, with aromatic d_{C-H} distances of 0.95 Å and $U_{iso(H)} = 1.2U_{eq(C)}$. **8a·2-($CH_3OH$)**: (Nonius, CAD4; sealed tube, Nonius FR590; $T = 163$ K; correction for decay was applied). All hydrogen atoms were found in the Fourier maps and were allowed to refine freely. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-664635 (**2a**), CCDC-664636 **[4a·(CH_2Cl_2)]**, CCDC-664637 (**6a**), and CCDC-664638 **[8a·(CH_3OH)]**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: (+44)1223−336-033. E-mail: deposit@ccdc.cam.ac.uk or at www.ccdc.cam.ac.uk/conts/retrieving.html).

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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