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Reactivity of *cis*-$[Pd_4(\mu\text{-}X)_4\{\mu\text{-}C(C_6F_5)=NMe\}_4]$ (X = Cl, Br, I) towards neutral bidentate ligands

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Abstract

The complexes *cis*-$[Pd_4(\mu\text{-}X)_4\{\mu\text{-}C(C_6F_5)=NMe\}_4]$ (X = Cl, Br, I) react with neutral bidentate ligands L–L (L–L = 2,2′-bipyridine, *N,N,N′,N′*-tetramethylethylenediamine, or 1,2-bis(diphenylphosphino)ethane (Pd/L–L ratio 2/1) to give $[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2X_2(L\text{–}L)]$. These binuclear complexes (X = Cl) react with the ligands L–L to form the mononuclear complexes $[Pd\{C(C_6F_5)=NMe\}Cl(L\text{–}L)]$ containing a terminal pentafluorobenzimidoyl group. When the reaction is carried out in the presence of $NaClO_4$ the dinuclear cationic derivatives $[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2(L\text{–}L)_2](ClO_4)_2$ are formed. Their structures are discussed on the basis of ^1H and ^{19}F NMR data.

Introduction

We have published a preliminary report [1] on the diverse behaviour of imidoyl bridges towards neutral nucleophiles. The crown-shaped complex *cis*-$[Pd_4(\mu\text{-}Cl)_4\{\mu\text{-}C(C_6F_5)=NMe\}_4]$, now fully characterized [2,3] has been shown to react with monodentate ligands (including CNR or PPh_3) in Pd/L ratio 1/1 with cleavage of the chloro bridges to give dinuclear imidoyl-bridged complexes $[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2Cl_2L_2]$ [2]; an excess of L = CNR cleaves the imidoyl bridges to give terminal-imidoyl complexes *trans*-$[Pd\{C(C_6F_5)=NMe\}Cl(CNR)_2]$, whereas excess of L = PPh_3 causes extrusion of isonitrile to give *trans*-$[Pd(C_6F_5)Cl(PPh_3)_2]$ [4]. In this paper we present a full report on the reactions of the complexes *cis*-$[Pd_4(\mu\text{-}X)_4\{\mu\text{-}C(C_6F_5)=NMe\}_4]$ (X = Cl, Br, I) towards the bidentate ligands 2,2′-bipyridine (bipy) *N,N,N′,N′*-tetramethylethylenediamine (tmen) and 1,2-bis(diphenylphosphino)ethane (dppe).

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Results and discussion

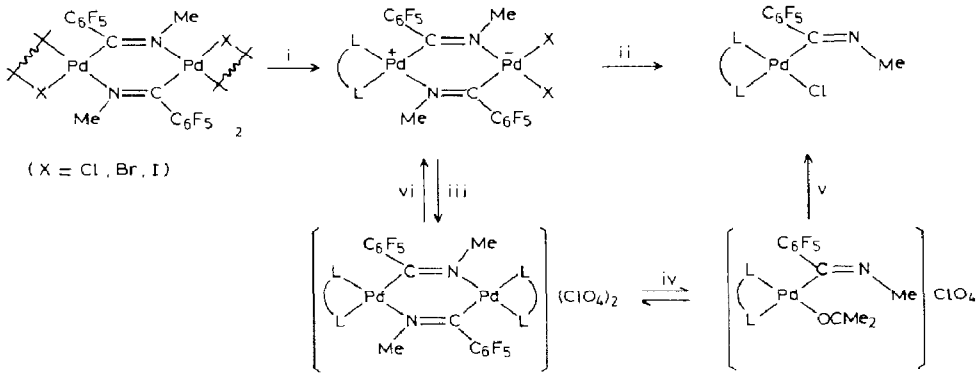
When the crown-shaped tetranuclear complex *cis*-$[Pd_4(\mu\text{-}Cl)_4\{\mu\text{-}C(C_6F_5)=NMe\}_4]$ is treated in acetone with 2,2′-bipyridine (Pd/bipy ratio 1/1), a yellow precipitate is quickly formed; its analytical data indicate a Pd/bipy ratio 2/1. Further reaction with the remaining bipy, leading eventually to redissolution of the initial precipitate, takes place only slowly, and work-up of the resulting solution leads to the isolation of a compound with a Pd/bipy ratio 1/1. Since the insolubility of the former product makes it unsuitable for structural studies, tmen and dppe were also used in place of bipy, in the hope of obtaining more soluble compounds.

We found (see Scheme 1) that in a general reaction (i), the complexes *cis*-$[Pd_4(\mu\text{-}X)_4\{\mu\text{-}C(C_6F_5)=NMe\}_4]$ react with bipy or tmen in acetone or with dppe in ether (Pd/L–L ratio 2/1) to give $[Pd_2\{\mu\text{-}C(C_6F_5)=NMe\}_2X_2(L\text{–}L)]$. The ^{19}F NMR spectra of the soluble compounds IV and VII (see Table 2) displayed two sets of five signals corresponding to two inequivalent C_6F_5 rings, each with five inequivalent F atoms.

In the light of our earlier results [2,4], this means that both imidoyl groups are bridging, and furthermore they are non-equivalent. This, along with the non-conducting behaviour of the compounds and the chelating nature of L–L, leads to the formulation of the complexes shown in Scheme 1. In this formulation, and with the imidoyl group regarded as a neutral ligand at the N-end as a monoanionic ligand at the C-end, the complexes are formally zwitterionic, the Pd atom bearing the L–L ligand having a positive formal charge and that bearing the two Cl ligands a negative formal charge.

The X-ray structure determination on complex IV [1] revealed a significant difference between the two Pd–C(imidoyl) distances in the complex, and this can be attributed to some multiple bond character in the $\overline{Pd}$–C bond which would be absent in the $\overset{+}{Pd}$–C bond [5].

These dinuclear complexes react (although slowly) with further L–L (ii) to give the mononuclear complexes $[Pd\{C(C_6F_5)=NMeC\}(L\text{–}L)]$, which are non-conducting in solution and display only three signals (2/1/2) in the ^{19}F NMR spectrum, as



Scheme 1. (i) + L–L = bipy, tmen, in acetone; + L–L = dppe, in Et_2O. (ii) + L–L = bipy, tmen, in acetone; + L–L = dppe, in Et_2O. (iii) + $NaClO_4$, + L–L = bipy, tmen, dppe, in acetone. (iv) in acetone, L–L = bipy. (v) + KCl, L–L = bipy, in acetone. (vi) + LiCl, L–L = tmen, in acetone.

expected for a terminal pentafluorobenzimidoyl group [4]. The formation of these mononuclear complexes deserves comment.

When using monodentate ligands we have observed that the imidoyl double bridge is quite stable, and N-donor ligands do not cleave it. PR_3 or CNR ligands will cleave the bridges, but only the latter are able to stabilize the terminal pentafluorobenzimidoyl group, whereas cleavage with PPh_3 leads to extrusion of CNMe and formation of a $Pd-C_6F_5$ bond [4]. In the present work we have found that both N- and P-donor chelate ligands can cleave these bridges and, more interestingly, stabilize the terminal pentafluorobenzimidoyl group, although under more forcing conditions some extrusion of CNMe has been detected (mainly with the dppe derivatives).

In addition it should be noted that whereas the first L–L molecule causes asymmetric cleavage of the Cl-bridges, without ligand rearrangement, to give dinuclear complexes in a fast process, the second L–L ligand is incorporated only slowly to give the mononuclear complexes, and this process involves a rearrangement of ligands. Since the fastest and easiest reaction occurs with the bipy complex I, which is the least soluble, the reason for the slow rate of the second process is not the low solubility of the dinuclear zwitterionic complex.

In contrast, the zwitterionic complexes I, IV, and VII react with one mol of L–L in the presence of $NaClO_4$ (iii) to give the dinuclear cationic complexes XIII, XIV, and XV, which behave in acetone solutions as 2/1 electrolytes. Complex XIII was recovered from CH_2Cl_2 as XIIIa and from acetone as XIIIb; i.e. in each case the compound retained one mol of solvent per palladium atom, as shown by the analytical results, ^1H NMR spectroscopy, and, in the case of XIIIb, IR spectroscopy (ν(C=O) 1718, 1710 cm^{-1}).

The IR spectra of Nujol mulls of the cationic complexes XIII, XIV, and XV were all consistent with their formulation as imidoyl-bridged complexes according to their ν(C=N) wavenumbers; XIIIa and XIIIb showed identical spectra except for the ν(C=O) absorption in the complex with acetone of crystallisation.

The ^{19}F NMR spectra, which were recorded in deuteroacetone because of the low solubility of the complexes in $CDCl_3$, were more interesting. Complexes XIV and XV showed a pattern of five signals with equal integrals, as expected from the chemical equivalence of the two C_6F_5 groups and the chemical inequivalence of the five F-atoms in a bridging pentafluorobenzimidoyl group. Unexpectedly both XIIIa and XIIIb in hexadeuteroacetone showed the same pattern of only three signals (2/1/2) found for terminal pentafluorobenzimidoyl groups; only when the spectrum of complex XIIIa was recorded in CH_2Cl_2 in which it is slightly soluble) could the expected five-signal pattern be observed. This suggests that whereas all the complexes have a binuclear structure in the solid state or in non-coordinating solvents, acetone is able to split the generally strong imidoyl bridges in complex XIII (L–L = bipy) but not when L–L = tmen, dppe (complexes XIV and XV).

This different behaviour of complex XIII was reflected in its reactivity. Thus complex XIII reacted with KCl in acetone to give the mononuclear complex X (by reaction v). In contrast, complex XIV did not react appreciably with KCl, and when it was treated with the more soluble LiCl the binuclear zwitterionic complex IV was the main product (by reaction iv). A similar experiment, could not be carried out with complex XV because of the low stability of the dppe complexes in solution.

The transformation of the zwitterionic complexes I, IV, and VII into the

(*Continued on p. 274*)

Table 1. Analytical data yields and, relevant IR data

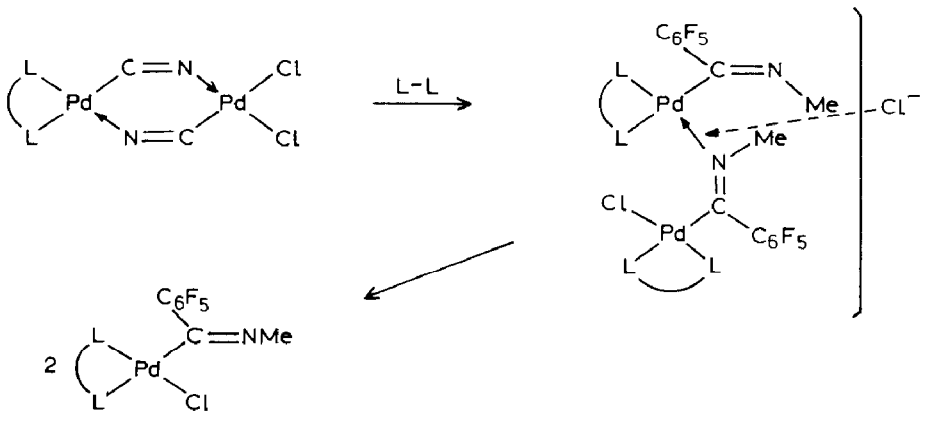
Compound	Analysis (Found (calcd.)(%))			Yield (%)	ν(C=N) (cm^{-1})	ν(Pd–Cl) (cm^{-1})
	N	C	H			
[(bipy)Pd{μ-C(C_6F_5)=NMe}$_2$$PdCl_2$] (I)	6.49	36.30	1.85	68	1578	318, 258
	(6.54)	(36.48)	(1.65)			
[(bipy)Pd{μ-C(C_6F_5)=NMe}$_2$$PdBr_2$] (II)	6.02	33.37	1.72	75	1575	
	(5.93)	(33.05)	(1.49)			
[(bipy)Pd{μ-C(C_6F_5)=NMe}$_2$$PdI_2$] (III)	5.31	30.43	1.62	60	1573	
	(5.39)	(30.06)	(1.36)			
[(tmen)Pd{μ-C(C_6F_5)=NMe}$_2$$PdCl_2$] (IV)	6.89	32.65	2.87	66	1584	314, 282
	(6.87)	(32.38)	(2.72)			
[(tmen)Pd{μ-C(C_6F_5)=NMe}$_2$$PdBr_2$] (V)	6.13	30.00	2.39	55	1581	
	(6.19)	(29.20)	(2.45)			
[(tmen)Pd{μ-C(C_6F_5)=NMe}$_2$$PdI_2$] (VI)	5.26	26.66	2.16	90	1578	
	(5.61)	(26.45)	(2.22)			
[(dppe)Pd{μ-C(C_6F_5)=NMe}$_2$$PdCl_2$] (VII)	2.48	45.16	3.16	94	1580	329, 310
	(2.55)	(45.93)	(2.75)			
[(dppe)Pd(μ-C_6F_5)=NMe}$_2$$PdBr_2$] (VIII)	2.24	43.19	2.81	82	1576	
	(2.36)	(42.49)	(2.55)			
[(dppe)Pd{μ-C(C_6F_5)=NMe}$_2$$PdI_2$] (IX)	1.94	39.25	2.93	55	1571	
	(2.19)	(39.37)	(2.36)			
[Pd{C(C_6F_5)=NMe}Cl(bipy)] (X)	7.93	42.53	2.27	77	1622	322
	(8.30)	(42.68)	(2.19)			
[Pd{C(C_6F_5)=NMe}Cl(tmen)] (XI)	9.18	35.89	4.42	60	1619	323
	(9.01)	(36.07)	(4.11)			
[Pd{C(C_6F_5)=NMe}Cl(dppe)] (XII)	1.57	54.90	4.13	82	1601	286
	(1.87)	(54.57)	(3.64)			
[Pd_2(μ-C(C_6F_5)=NMe}$_2$(bipy)$_2$](ClO_4)$_2$·2CH_2Cl_2 (XIIIa)	6.47	34.59	1.91	46	1573	
	(6.41)	(34.84)	(2.00)			
[Pd_2(μ-C(C_6F_5)=NMe}$_2$(bipy)$_2$](ClO_4)$_2$·2Me_2CO (XIIIb)	6.55	39.87	2.70	70	1573	
	(6.69)	(40.15)	(2.73)			
[Pd_2(μ-C(C_6F_5)=NMe}$_2$(tmen)$_2$](ClO_4)$_2$ (XIV)	7.73	31.23	3.34	75	1565	
	(7.93)	(31.72)	(3.61)			
[Pd_2(μ-C(C_6F_5)=NMe}$_2$(dppe)$_2$](ClO_4)$_2$ (XV)	1.55	50.53	3.95	63	1558	
	(1.72)	(50.27)	(3.35)			

Table 2

NMR data (shifts (δ, ppm) relative to $CFCl_3$ for ^{19}F and 85% aqueous H_3PO_4 for ^{31}P)

Compound	F^2(m)	F^6(m)	F^4(t)	F^3(m)	F^5(m)	solvent	P^1, P^2	$^2J(P^1-P^2)$ (Hz)
[(tmen)Pd{μ-C(C_6F_5)=NMe}$_2$$PdCl_2$] (IV)	−135.2; −138.9	−141.2; −142.3	−150.8; −154.3	~ −159.5	~ −161.9	[a]		
[(dppe)Pd{μ-C(C_6F_5)=NMe}$_2$$PdCl_2$] (VII)	−136.2; −137.2	−142.1; −144.9	−155.2; −155.9	−160.6; −162.6	−161.8; −163.0	[a]	48.7(d),53.8(d)	25.7
[Pd{C(C_6F_5)=NMe}Cl(bipy)] (X)	−141.5		−157.8	−163.5		[a]		
[Pd{C(C_6F_5)=NMe}Cl(tmen)] (XI)	−139.9		−156.9	−163.3		[a]		
[Pd{C(C_6F_5)=NMe}Cl(dppe)] (XII)	−140.5		−159.2	−165.0		[a]	33.3(m),49.1(d) [d]	
[Pd_2(μ-C(C_6F_5)=NMe}$_2$(bipy)$_2$](ClO_4)$_2$·2CH_2Cl_2 (XIIIa)	−138.4;	−139.4	−148.3	−158.7;	−159.3	[b]		
[Pd_2(μ-C(C_6F_5)=NMe}$_2$(bipy)$_2$](ClO_4)$_2$·2$OCMe_2$ (XIIIb)	−136.9		−150.0	−159.5		[c]		
[Pd_2(μ-C(C_6F_5)=NMe}$_2$(tmen)$_2$](ClO_4)$_2$ (XIV)	−137.7;	−138.8	−150.7	−159.0;	−159.5	[c]		
[Pd_2(μ-C(C_6F_5)=NMe}$_2$(dppe)$_2$](ClO_4)$_2$ (XV)	−134.1;	−139.0	−153.1	~ −159.6;	~ −159.8	[c]	42.2(d),52.9(d)	21.9

[a] $CDCl_3$. [b] CH_2Cl_2. [c] Acetone-d_6. [d] Decomposition during the recording produces blurried signals.



Scheme 2

mononuclear complexes X, XI, and XII in the presence of L–L involves a rearrangement of the Cl ligands. The sequence of reactions iii, iv, and v observed for L–L = bipy suggests that the rearrangement involved in process ii may follow a similar path, i.e., displacement of the two Cl ligands by L–L to give a cationic dinuclear complex (with Cl^- instead of ClO_4^- as counterion) followed by bridge-splitting by the Cl^- counterions. However, the fact that process v does not take place for L–L = tmen even in the presence of a high concentration of Cl^-, the zwitterionic complex being regenerated, coupled with the fact that this latter complex IV only gives complex XI when a large excess of tmen is used, rather suggests that the step that initiates the rearrangement is the cleavage of the bridge by the L–L ligand, as depicted in Scheme 2. The imidoyl bridges seem to be more easily cleaved when L–L = bipy (as observed in the cationic complexes), and consequently they react faster, and even with a stoicheiometric amount of L–L.

The analytical results, yields and relevant IR absorptions of the complexes prepared are given in Table 1; in addition to the IR absorptions listed in Table 1 other absorptions, associated with the C_6F_5 group, are found near 1650, 1515, 1490, 1125, 980, 950, 825–800 cm^{-1}. It should be noted that whereas ν(C=N) for bridging imidoyls appear in the range 1585–1558 cm^{-1}, terminal imidoyls show ν(C=N) at higher wavelengths, in the range 1622–1601 cm^{-1}. The ^{19}F and ^{31}P NMR data are listed in Table 2.

Experimental

The C, H, and N analyses were carried out with a Perkin–Elmer 240-B microanalyser. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer with Nujol mulls between polyethylene plates. ^1H, ^{19}F and ^{31}P NMR spectra were recorded on a Varian XL-200 instrument (200 MHz for ^1H). Molecular weights were determined in $CHCl_3$ solution with a Perkin–Elmer 115 apparatus. Conductivities were measured in approx. 5×10^{-4} *M* acetone solution with a Philips PW 9501/01 conductimeter.

Typical preparations of the complexes are described below.

[Pd_2\{μ-$C(C_6F_5)$=NMe\}$_2Cl_2$(bipy)] (I). To a stirred suspension of 200 mg of [Pd_4(μ-$C(C_6F_5)$=NMe}$_4Cl_4$] in acetone (30 cm^3) were added 44.7 mg of 2,2′-bi-

pyridine (Pd/bipy 2/1), yellow precipitate appeared, and this was filtered off, washed with cold acetone, and dried.

[Pd_2\{μ-C(C_6F_5)=NMe\}$_2Cl_2$(tmen)] (IV). To a stirred suspension of 444.5 mg of [Pd_4\{μ-C(C_6F_5)=NMe\}$_4Cl_4$] in 40 cm^3 of acetone were added 96 μl of *N,N,N′,N′*-tetramethylethylene diamine (Pd/tmen = 2/1. A yellow precipitate was formed. The mixture was stirred for 30 min and then the acetone was evaporated to 5 cm^3, ethanol (20 cm^3) was added, and the yellow product was filtered off, dried, and recrystallized from dichloromethane.

[Pd_2\{μ-C(C_6F_5)=NMe\}$_2Cl_2$(dppe)] (VII). To a stirred suspension of 200 mg of [Pd_4\{μ-C(C_6F_5)=NMe\}$_4Cl_4$] in diethyl ether (20 cm^3) were added 113.9 mg of 1,2-bis(diphenylphosphino)ethane (Pd/dppe 2/1). A yellow precipitate was formed. The mixture was stirred for 6 h and the yellow product was filtered off, washed with diethyl ether, and dried.

[Pd\{C(C_6F_5)=NMe\}Cl(bipy)] (X). Method A: To a suspension of complex I (50 mg) in acetone (20 cm^3) was added an excess of 2,2′-bipyridine (100 mg) and the mixture was stirred for 6 h. Evaporation of the resulting yellow solution and addition of diethyl ether (20 cm^3) afforded a pale-yellow solid, which was filtered off, washed with diethyl ether to remove any free bipy, and air dried.

Method B: An excess of KCl (150 mg) was added to a solution of complex XIIIa (70 mg) in acetone (20 cm^3) and the mixture was stirred for 12 h. Then the mixture was evaporated to dryness and the residue was extracted with CH_2Cl_2 (40 cm^3). The CH_2Cl_2 solution was filtered then evaporated to dryness and diethyl ether (10 cm^3) was added, to give a pale yellow solid, which was filtered off, washed with diethyl ether, and air dried.

[Pd\{C(C_6F_5)=NMe\}Cl(tmen)] (XI). To a suspension of complex IV (6.3 mg) in acetone (20 cm^3) was added a large excess *N,N,N′,N′*-tetramethylethylenediamine (1.5 cm^3). The mixture was stirred for 24 h to give a yellow solution, which was evaporated to dryness. Addition of ethanol (10 cm^3) gave a pale yellow solid, which was filtered off, washed with ethanol, and air dried.

[Pd\{C(C_6F_5)=NMe\}Cl(dppe)] (XII). To a stirred suspension of [Pd_4\{μ-C(C_6F_5)=NMe\}$_4Cl_4$] (200 mg) in diethyl ether (25 cm^3) was added stoicheiometric amount of 1,2-bis(diphenylphosphino)ethane (227.7 mg), and the mixture was stirred for 12 h. The resulting yellow precipitate was filtered off, washed with diethyl ether, and air dried.

[Pd_2\{μ-C(C_6F_5)=NMe\}$_2$(bipy)$_2$](ClO_4)$_2$ · 2CH_2Cl_2 (XIIIa). To a suspension of I (200 mg) in CH_2Cl_2 (30 cm^3) were added 37 mg of 2,2′-bipyridine and 70 mg of dry $NaClO_4$. Upon stirring the precipitate of IV slowly dissolved. The mixture was stirred for 2 days, and then filtered to remove the NaCl and the excess of $NaClO_4$. The solution was evaporated to 5 ml to give a yellow solid, which was filtered off, washed with cold CH_2Cl_2, and air dried.

[Pd_2\{μ-C(C_6F_5)=NMe\}$_2$(bipy)$_2$](ClO_4)$_2$ · 2Me_2CO (XIIIb). Complex XIIIa (200 mg) was dissolved in acetone (30 ml). Evaporation to a small volume and cooling in the freezer afforded complex XIIIb as yellow crystals, which were filtered off and air dried.

[Pd_2\{μ-C(C_6F_5)=NMe\}$_2$(tmen)$_2$](ClO_4)$_2$ (XIV). 200 mg of IV in acetone (30 cm^3) were stirred with 40 ml of *N,N,N′,N′*-tetramethylethylenediamine and 70 mg of $NaClO_4$ for 8 h. The mixture was evaporated to dryness and the residue was extracted with dichloromethane (100 cm^3). The solution was filtered then evaporated

to 10 ml to give a yellow microcrystalline solid, which was filtered off, washed with ethanol, and dried. Λ_M 210 $ohm^{-1}\,cm^2\,mol^{-1}$.

[Pd$_2$\{μ-C(C$_6$F$_5$)=NMe\}$_2$(dppe)$_2$](ClO$_4$)$_2$ (XV). Complex VII (150 mg) in acetone (30 cm^3) was stirred with 55 mg of 1,2-bis(diphenylphosphino)ethane and 100 mg of $NaClO_4$ for 2 h. The solvent was evaporated off and the residue extracted with 50 cm^3 of CH_2Cl_2. The filtered extract was evaporated to dryness and 10 cm^3 of ethanol were added, to give a white precipitate, which was filtered off, washed with ethanol, and air dried. Λ_M 229 $ohm^{-1}\,cm^2\,mol^{-1}$.

Reaction of complex XIV with LiCl. To a solution of complex XIV (100 mg) in acetone (30 cm^3) was added an excess of LiCl (150 mg). The mixture was stirred for 36 h then the suspended yellow solid was filtered off, washed with water (2 × 20 cm^3) then with ethanol, to give 20 mg of complex IV. From the mother liquors some of the starting material (complex XIV) was recovered.

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