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Synthesis, Structures, Ligand Substitution Reactions, and Electrochemistry of the Nitrile Complexes *cis*-$[Ru(dppm)_2Cl(NCR)]^+$ PF_6^- (dppm = Bis(diphenylphosphino)methane, R = CH_3, C_2H_5, ^{t}Bu, Ph)

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Abstract. Isomerically pure nitrile complexes *cis*-$[Ru(dppm)_2Cl(NCR)]^+$ (**2a–d**) are formed upon chloride displacement from *cis*-$[Ru(dppm)_2Cl_2]$ (**1**) or, alternatively, by ligand substitution from the acetonitrile complex **2a**. This latter approach does also allow for the introduction of pyridine (**3a,b**), heptamethyldisilazane (**4**) or isonitrile ligands (**5**). All complexes are obtained as the configurationally stable *cis*-isomers. Only *cis*-$[Ru(dppm)_2Cl(CN^tBu)]^+$ slowly isomerizes to the *trans* from. The solid state structures of the CH_3CN, C_2H_5CN and the *trans*-^{t}BuNC complexes were established by X-ray crystallography. Electrochemical investigations of the nitrile complexes **2a–d** show in addition to a chemically reversible one-electron oxidation an irrversible reduction step. In CH_2Cl_2 solution, *cis*- and *trans*-$[Ru(dppm)_2Cl_2]$ have been identified as the final products of the electrochemically induced reaction sequence.

Synthese, Strukturen, Ligandenaustauschreaktionen und Elektrochemisches Verhalten der Nitrilkomplexe *cis*-$[Ru(dppm)_2Cl(NCR)]^+$ PF_6^- (dppm = Bis(diphenylphosphino)methan, R = CH_3, C_2H_5, ^{t}Bu, Ph)

Inhaltsübersicht. Isomerenreine Nitrilkomplexe *cis*-$[Ru(dppm)_2Cl(NCR)]^+$ (**2a–d**) sind, ausgehend von *cis*-$[Ru(dppm)_2Cl_2]$ (**1**), durch Chloridaustausch oder durch Substitution des Acetonitrilliganden von **2a** in einfacher Weise zugänglich. Die zweite Methode erlaubt auch die Einführung von Pyridin- (**3a,b**), Amin- (**4**) oder Isonitrilliganden (**5**), wobei die Substitutionsprodukte als konfigurationsstabile *cis*-Isomere erhalten werden. Lediglich im Falle von *cis*-$[Ru(dppm)_2Cl(CN^tBu)]^+$ tritt Isomerisierung zur *trans*-Form ein. Die Strukturen der Komplexkationen im CH_3CN-, C_2H_5CN- und im *trans*-^{t}BuNC-Komplex wurden zusätzlich durch Röntgenbeugung bestimmt. Elektrochemische Untersuchungen an den Nitrilkomplexen **2a–d** zeigen neben einer chemisch reversiblen Einelektronenoxidation einen chemisch jeweils irreversiblen Reduktionsschritt. In CH_2Cl_2-Lösung konnten *cis*- und *trans*-$[Ru(dppm)_2Cl_2]$ als Folgeprodukte der elektrochemisch initiierten Reaktionssequenz identifiziert werden.

Introduction

Nitriles constitute an important ligand class in organometallic chemistry. They form stable complexes with a wide variety of transition metals [1] and may stabilize the metal in various oxidation states [2–5]. Since nitrile ligands are easily replaced by other ligands, complexes $[ML_n(NCR)_m]^{x+}$ are valuable sources of coordinatively unsaturated fragments $[ML_n]^{x+}$. Recent applications in the area of ruthenium chemistry have mainly focused on bis- or tris-acetonitrile arene or cyclopentadienyl half-sandwich complexes $[(arene)Ru(CH_3CN)_2Cl]^+$ [6–8] or $[Cp^sRu(CH_3CN)_3]^+$ (Cp^s = C_5H_5, $C_5(CH_3)_5$) [9–11]. Nitrile substituted bis(diphosphine) derivatives $[XRu(L_2)_2(NCR)]^+$ (X = anionic ligand) have, however, received much less attention. *cis*-$[Ru(dppe)_2Cl(NCR)]^+$ (R = Me, Ph, 2,6-$(MeO)_2C_6H_3$, dppe = $Ph_2PC_2H_4PPh_2$) are formed upon addition of the respective nitrile to the five-coordinate $[ClRu(dppe)_2]^+$ [12]. With more bulky diphosphine ligands like $(C_6H_{11})_2PC_2H_4P(C_6H_{11})_2$ (dcpe) only the *trans*-isomers $[ClRu(L_2)_2(NCCH_3)]^+$ are formed [13]. *cis*-$[Ru(dppm)_2Cl(NCCH_3)]^+$ (dppm = $Ph_2PCH_2PPh_2$, **2a**) has briefly been mentioned, but only analytical and electrochemical data have been published [4]. We report here the easy, high-yield syntheses of cationic mononitrile complexes *cis*-$[Ru(dppm)_2Cl(NCR)]^+$ PF_6^- (R = Me, **2a**, R = Et, **2b**,

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R = ^{t}Bu, **2c**, Ph, **2d**) and of the dicationic bis(nitrile) complex *cis*-$[Ru(dppm)_2(NCCH_3)_2]^{2+}(PF_6^-)_2$ (**6**). Starting from **2a** we have prepared several substitution products containing nitrogen or isonitrile donors in high yields. The solid state structures of **2a**, **2b** and *trans*-$[Ru(dppm)_2Cl(CN^tBu)]^+PF_6^-$ (***trans-5***) have additionally been examined by X-ray crystallography.

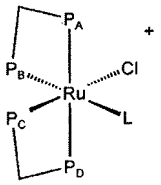
Results and Discussion

1 Syntheses and Properties

In 1982 *Sullivan* and *Meyer* reported the easy dissociation of chloride from *cis*-$[RuCl_2(dppm)_2]$ (**1**) in acetonitrile solution and the selective formation of *cis*-$[Ru(dppm)_2Cl(CH_3CN)]^+$ (**2a**) as evidenced by cyclic voltammetry [4]. We observed by ^{31}P-NMR spectroscopy that upon addition of CD_3CN to a solution of **1** in CD_2Cl_2 the A_2X_2 spin system of **1** is immediately replaced by an ABMX pattern, indicating the formation of **2a**. Other nitriles RCN behave similarly as was shown for propionitrile (R = C_2H_5), pivalonitrile (R = ^{t}Bu) or benzonitrile (R = Ph). More detailed NMR experiments indicated that for aliphatic nitriles a 540 fold excess is sufficient to selectively form the mononitrile complexes **2a–c** without concomitant formation of bis-substitution products $[Ru(dppm)_2(NCR)_2]^{2+}$.

Based on these results we developped an easy one-pot synthesis rendering mononitrile complexes **2** in more than 90% isolated yields. The benzonitrile complex **2d** was purified by fractional crystallization from $CH_3NO_2/C_2H_4Cl_2$ (3:1) and obtained in 62% overall yield. Alternatively, the acetonitrile complex **2a** may be used as starting material for complexes containing other nitrile ligands. Thus, stirring CH_2Cl_2 solutions of **2a** in the presence of 20 equivalents of free nitrile afforded the substitution products **2b, c** in high purity and excellent yields. The ready displacement of coordinated nitriles from similar ruthenium complexes with only little selectivity with respect to the incoming nitrile has already been observed [12]. This latter method may also be applied to pyridine (**3a,b**), amine (**4**) or isonitrile ligands (**5**), rendering **2a** a readily available and stable precursor to complexes $[Ru(dppm)_2ClL]^+$.

Complexes **2** and **3** are obtained as the pure, stable *cis*-isomers. This follows directly from the four separate resonance signals in their ^{31}P-NMR spectra. They consist of eight individual lines each forming an overall ABMX pattern. Two signals display characteristically large *trans* couplings of ca. 300 Hz and two much smaller coupling constants of some 30 to 40 Hz due to coupling to two inequivalent *cis*-disposed phosphorus atoms. They are assigned to the apical phosphorus nuclei P_A and P_D (see Chart 1). The two remaining resonance signals are coupled by three different coupling constants ranging from 22 to 32 Hz, characteristic of mutually *cis*-disposed P-atoms. They are assigned to the equatorial phosphorus nuclei P_B and P_C, taking the plane containing the ligand L, the chloride, P_B and P_C as the equatorial plane. All ^{31}P-NMR data are collected in Table 1. Our assignment is based on the assumption that the resonance signals of the P-atom *trans* to the ligand L and that of the apical P-atom atom covalently linked to it are more susceptible to changes in L than the signals of the other P-atoms. The low symmetry of the *cis*-products is also evident from the ^{1}H and ^{13}C-NMR spectra. Thus, each of the four methylene protons of the dppm bridge gives a multiplet signal in the ^{1}H-NMR spectrum. A highly complex pattern is observed in the arene region. In their ^{13}C-NMR spectra all *cis*-complexes display two occasionally overlapping multiplet signals for the methylene carbons of the dppm ligands. In the aromatic region a multitude of individual signals, many split into multiplet patterns by coupling to phosphorus nuclei are detected and further assignment was not possible. We were not able to observe the resonance signals for the nitrile or isonitrile carbon atoms. The former are expected to fall into the aromatic region while the signals of the isonitrile carbons are probably split into complex multiplets by coupling to phosphorus [14].



Complexes **3b** and **4** could only be obtained as somewhat impure samples. For the amine complex **4**, some trans-isomer could not be separated even upon multiple reprecipitation as evidenced by a singlet at δ = –6.60 in the ^{31}P-NMR spectrum. The 4-DMAP complex **3b** is prone to dismutation, especially in more polar solvents. Thus, upon attempted recrystallization from acetone/ethanol considerable amounts of *cis*-$[Ru(dppm)_2Cl_2]$ (**1**) and *cis*-$[Ru(dppm)_2(4\text{-DMAP})_2]^{2+}$ are formed. The latter is characterized by two triplets (J = 39.1 Hz) at δ = 11.96 and –8.65 in the ^{31}P-NMR spectrum.

The isonitrile complex *cis*-**5** slowly isomerizes to the *trans*-isomer, even under ambient conditions [15]. In order to isolate nearly pure *cis*-**5**, the reaction had to be run in an ice-bath with short reaction times. After crystallization from nitromethane/dichloroethane pure *trans*-**5** was obtained as very pale orange plates. In *cis*-**5** and *trans*-**5** the $[Ru(dppm)_2Cl]^+$ fragment exhibits markedly different electron releasing properties toward the π acidic isonitrile ligand as may be inferred from IR-spectroscopy. Thus, the *cis*-isomer displays an

Table 1 ^{31}P-NMR data of compexes *cis*-[Ru(dppm)$_2$ClL]$^{+a)}$

L	δ P_A	δ P_B	δ P_C	δ P_D	J (P_AP_D)	J (P_AP_B)	J (P_AP_C)	J (P_BP_C)	J (P_BP_D)	J (P_CP_D)	
CH_3CN	–19.39	–6.10	0.36	–25.16	322.2	43.6	24.2	29.0	31.8	44.7	**2a**
EtCN	–17.59	–4.21	2.09	–26.05	322.7	43.7	24.1	28.9	31.6	44.9	**2b**
^{t}BuCN	–16.97	–2.36	3.03	–23.32	322.0	44.8	24.3	29.2	31.2	45.2	**2c**
PhCN	–19.55	–6.97	–0.42	–26.00	321.4	43.5	23.7	28.8	31.5	44.9	**2d**
Py$^{b)}$	–16.02	–1.94	3.67	–22.71	321.9	44.0	24.5	29.3	31.2	44.9	**3a**
4-DMAP	–17.68	–2.16	3.95	–21.53	326.6	29.8	26.5	26.3	31.8	43.0	**3b**
$MeN(SiMe_3)_2$	–20.27	–3.19	2.66	–22.73	313.9	27.6	28.8	27.0	31.1	44.3	**4**
^{t}BuNC	–14.01	–22.90	–3.45	–27.71	295.0	36.2	22.4	24.8	30.2	45.3	**5**

[a] Spectra recorded in CD_2Cl_2; [b] in CD_3NO_2

intense C≡N stretch at 2157 cm^{-1}, i.e. at an almost identical value as the free nitrile itself. In *trans*-**5**, this band is shifted to 2127 cm^{-1}. This indicates a somewhat higher degree of back-bonding in *trans*-**5** as a consequence of the disposition of the chloride π donor trans to the isonitrile π acceptor. The geometrical preferences of octahedral complexes $[MP_4LL']^{n+}$ depend on the electronic and steric properties of the ligands, the metal center and its oxidation state [4, 16–18] and, in the case of chelating ligands, also on the size of the chelate ring. As a general rule the preferred arrangement results when the more powerful π acceptors (dppm P-atoms in **2**–**4**, CN^{t}Bu in **5** or CO) are *trans* to the π donors (Cl) or the weaker π acceptors (NCR, pyridines, amines). Thus, for complexes $[M(L_2)_2ClL]^{n+}$ (M = Re, L = dppe, n = 0, M = Ru, L = dppm, n = 1) *cis*-isomers are preferred if L is a weak π-acid [16], while for stronger π acceptors such as isonitrile or carbonyl ligands the trans-isomer is thermodynamically more stable [17 b, 18, 19].

We have also synthesized the bis(acetonitrile) complex $[Ru(dppm)_2(NCCH_3)_2]^{2+}$ $(BF_4^-)_2$ (**6**) by Ag^+ assisted chloride abstraction in the presence of acetonitrile. Our attempts to prepare the mononitrile complex **2a** by reacting *cis*-[Ru(dppm)$_2$Cl$_2$] (**1**) with only one equivalent of $AgBF_4$ invariably produced mixtures of **2a** and **6**. **6** is obtained as exclusively the *cis*-isomer, again in accord with its rhenium (I) counterpart [17 a]. The CH_3CN ligands in **6** are considerably more resistant toward substitution than the single CH_3CN ligand in **2a**. Thus, upon treatment of **6** with a 10 fold excess of ^{t}BuNC only traces of a new species exhibiting an AMNX pattern in the ^{31}P-NMR spectrum, most likely $[Ru(dppm)_2(NCCH_3)(CN^tBu)]^{2+}$, were detected besides unchanged **6**. In view of this result, the chloride abstraction from **1** by Ag^+ in the presence of excess L (L denoting a neutral 2 electron donor) is the method of choice for the synthesis of complexes $[Ru(dppm)_2L_2]^{2+}$.

2 Crystal Structures

cis-$[Ru(dppm)_2Cl(NCR)]^+PF_6^-$ (**2a**: R = CH_3, **2b**: R = C_2H_5) and trans-$[Ru(dppm)_2Cl(CN^tBu)]^+PF_6^-$ (*trans*-**5**) appear to be the first nitrile and isonitrile complexes of ruthenium with a P_4X donor set to be characterized by X-ray structure analysis. Relevant bond lengths and angles for the complex cations in these compounds are collected in Table 2 and important details of the structure determinations are provided in Table 3. Plots of the cations are depicted as Figures 1–3. **2a,b** both crystallize in the polar space group Cc as a racemic mixture of the two enantiomers.

Table 2 Selected bond lengths (Å) and angles (deg) of the complex cations in **2a**, **2b** and *trans*-**5** (standard deviations in brackets)

	2a	**2b**	**5**
Ru–P1	2.3597(12)	2.331(2)	2.360(2)
Ru–P2	2.3190(12)	2.295(2)	2.360(2)
Ru–P3	2.3154(9)	2.297(2)	2.373(2)
Ru–P4	2.3595(12)	2.339(2)	2.394(2)
RuCl	2.4560(12)	2.435(2)	2.439(2)
RuL	2.082(3)	2.059(5)	1.932(7)
N–C01 or N–C9	1.131(5)	1.134(8)	1.155(8)
C01–C02 or N–C91	1.466(6)	1.426(7)	1.465(10)
P1–Ru–P2	70.70(5)	70.79(7)	109.27(7)
P1–Ru–P3	104.63(4)	104.44(6)	70.88(7)
P3–Ru–P4	71.30(4)	71.35(6)	108.72(7)
P2–Ru–P3	92.64(4)	92.51(6)	179.39(6)
P2–Ru–P4	103.44(5)	103.29(7)	71.09(7)
P1–Ru–P4	172.98(4)	172.86(7)	176.32(7)
P1–Ru–Cl	92.69(5)	92.78(7)	93.76(6)
P2–Ru–Cl	163.37(4)	163.56(5)	81.87(6)
P3–Ru–Cl	92.17(4)	92.09(6)	97.53(6)
P4–Ru–Cl	93.18(5)	93.13(7)	82.64(6)
P1–Ru–L	90.06(10)	90.2(2)	88.3(2)
P2–Ru–L	92.64(11)	93.3(2)	93.9(2)
P3–Ru–L	165.31(10)	165.4(2)	86.7(2)
P4–Ru–L	94.14(10)	94.2(2)	95.4(2)
Cl–Ru–L	86.62(10)	86.0(2)	175.7(2)
Ru–N–C01 or Ru–C9–N	178.4(4)	178.5(7)	176.7(7)
N–C01–C02 or C9–N–C91	176.7(7)	177.8(11)	178.0(6)

The structures of **2a,b** are highly reminiscent of that of the dichloro precursor complex *cis*-[Ru(dppm)$_2$Cl$_2$] (**1**) [20]. The coordination environment of ruthenium in compexes **2a,b** is that of a severely distorted octahedron. Major distortions are due to the acute chelate bite angles in the range of 70.70(5) to 71.35(6)° (72.1(3)° in **1**) imposed by the short methylene bridge. The axial phosphines are slightly bent toward the equatorial P-atoms such that the angles P_{ax}–Ru–P_{ax} are close to 173°. The Cl–Ru–N angles are somewhat

Table 3 Details of the structure determinations of **2a**, **b** and *trans*-**5**

	2a	**2b**	trans-5 · acetone
Empirical formula	$C_{52}H_{47}ClF_6NP_5Ru$	$C_{53}H_{49}ClF_6NP_5Ru$	$C_{58}H_{57}ClF_6NOPRu$
Formula weight	1091.28	1105.30	1189.42
Temperature	173(2) K	173(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic	monoclinic
Space group	Cc	Cc	P2(1)/c
Crystal size/mm	0.4×0.3×0.2	0.3×0.3×0.2	0.2×0.3×0.15
Unit cell dimensions			
a/Å	20.536(4)	20.222(5)	11.4586(18)
b/Å	12.314(3)	12.408(5)	25.442(4)
c/Å	20.904(4)	20.763(8)	19.6527(15)
β/deg	112.89(3)	112.93(3)	99.505(10)
Z	4	4	4
Volume/Å^3	4869.7(17)	4798(3)	5650.7(14)
ρ_{calcd}/g · cm^{-3}	1.488	1.530	1.398
Theta range (2θ)°	3.94–54.02	3.94 to 54.00	4.18 to 50.00
λ/Å	0.71073	0.71073	0.71073
Limiting indices	$-14 \le h \le 26$, $-15 \le k \le 13$, $-26 \le l \le 24$	$-13 \le h \le 25$, $-15 \le k \le 13$, $-26 \le l \le 25$	$0 \le h \le 13$, $0 \le k \le 30$, $-23 \le l \le 23$
Collected reflections	11851	10603	10369
Unique reflections	7693	7271	9849
R (int)	0.0464	0.0812	0.0682
μ(Mo-Kα)/mm^{-1}	0.602	0.612	0.526
R1 (all data)	0.0379	0.0676	0.1407
wR2 (all data)	0.0906	0.1211	0.1744
GooF on F^2	1.038	1.052	1.027
Flack parameter	–0.04(2)	–0.01(4)	–
Largest diff. peak/hole	0.550/–0.557	0.511/–0.420	0.912/–0.688

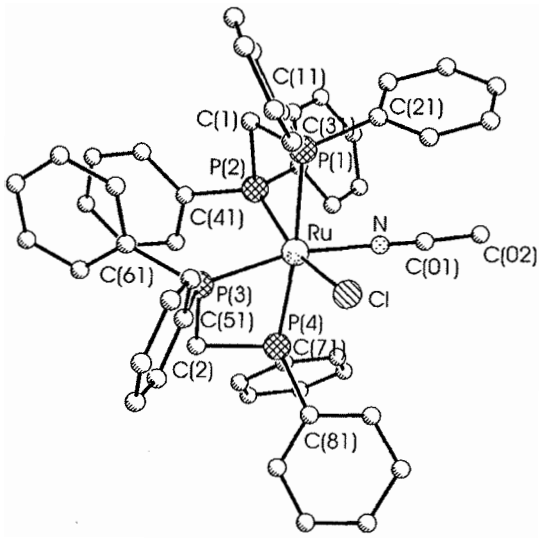


Fig. 1 Molecular structure of the cation of **2a** in the solid state.

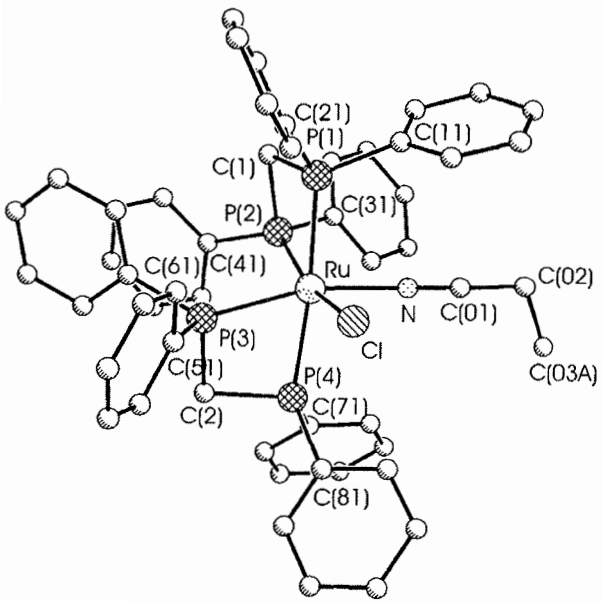


Fig. 2 Molecular structure of the cation of **2b** in the solid state (only one orientation for the disordered methyl group shown).

acute (86.6(1) and 86.0(2)°, respectively), while all other equatorial angles are larger than 90°, ranging from 92.09(7) to 93.3(2)°.

The Ru–P bond lengths vary from 2.331(2) to 2.360(1) Å for mutually trans disposed P-atoms and 2.295(2) to 2.319(1) Å for those P-atoms trans to the Cl or nitrile N atoms. The equivalent bond lengths in **1** are 2.335(10)–2.338(11) Å and 2.303(11)–2.318(10) Å, respectively [20]. The P-atoms *trans* to the nitrile ligand possess almost identical Ru–P bond lengths than those trans to chloride. This argues against any significant Ru dπ–N≡C pπ* back bonding in these cationic Ru^{II} complexes. *James* et al. have reached similar conclusions for $[Ru(dppb)(NCCH_3)_4]^{2+}$ and neutral *trans*-$[RuCl_2(NCCH_3)_4]$ [21]. In the former complex, the Ru–N bonds *trans* to the diphosphine ligand were found to be considerably longer than those to mu-

tually *trans* disposed nitrile ligands (2.108(2) and 2.120(2) Å vs 2.033(2) and 2.019(2) Å). The Ru–N bond lengths in **2a,b** are sligthly shorter (2.082(3) Å in **2a**, 2.059(5) in **2b**) and are rather similar to those found in monocationic half-sandwich nitrile complexes of ruthenium (2.040–2.063 Å) [6a, 7b, 11, 22]. The Ru–N≡C–C entity is essentially linear with N–C(sp) and C(sp)–C(sp^3) bond lengths of 1.131(5) or 1.134(8) and 1.466(6) or 1.426(7) Å, respectively.

trans-$[Ru(dppm)_2Cl(CN^tBu)]^+$ (***trans*-5**, see Fig. 3) closely resembles the neutral dichloride *trans*-$[Ru(dppm)_2Cl_2]$ [20] with somewhat larger Ru–P and Ru–Cl bond lengths for the cationic isonitrile complex (Ru–P: 2.360(2)–2.394(2) Å as compared to 2.340(1)–2.367(1) Å, Ru–Cl: 2.439(2) Å vs. 2.426(1) Å) in agreement with one chlorine being substituted by a π acceptor and the presence of an additional positive charge. Very similar bond parameters have been observed in the closely related *trans*-carbonyl $[Ru(dppm)_2(CO)Cl]^+$ (Ru–P = 2.369(3)–2.381(3) Å, Ru–Cl = 2.422(3) Å) [19]. The rather short Ru–C bond length of 1.932(7) Å compares well with those in other ruthenium complexes where the isonitrile ligand is also *trans* to an electron donor, e.g. *cis*-$[Ru(acac)_2(CNBu^t)_2]$ (1.910(6) and 1.920(5) Å) [23], or $[RuCl_2(P \sim O)_2(CNBu^t)]$ ($P \sim O = Ph_2PCH_2C_4H_7O_2$) (1.918(3) Å), where the isonitrile ligand is also *trans* to chloride [24]. The Ru–CN and the CNC-moieties are essentially linear (Ru–C≡N = 176.7(7)°, C≡N–C = 178.0(6)°. The C≡N and N–C bond lengths of 1.155(8) and 1.465(10) Å are well within the range of the other ruthenium-isonitrile complexes and deserve no further comment.

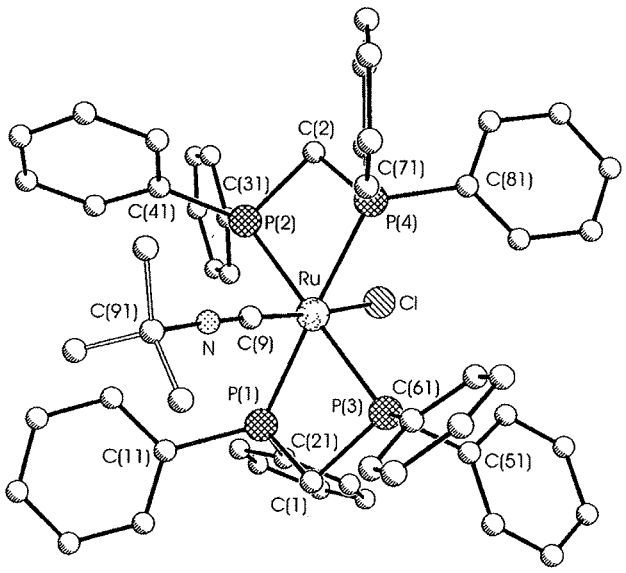


Fig. 3 Molecular structure of the cation of ***trans*-5** in the solid state (only one orientation for the disordered methyl groups shown).

3 Electrochemistry

The first oxidation of *cis*-$[Ru(dppm)_2Cl(NCCH_3)]^+$ has already been reported and assigned to the $Ru^{II/III}$ couple [4]. In agreement with these findings we observe a chemically reversible wave (peak current ratio $i_{p,c}/i_{p,a} = 1$) at potentials of ca. 1.00 V, depending on the solvent (see Table 4). Under our conditions, full chemical reversibility prevails even on the somewhat extended time scale of double-step chronoamperometry experiments [25]. From chronoamperometry we also determined the diffusion coefficient D of *cis*-$[Ru(dppm)_2Cl(NCCH_3)]^+$ as $1.05 \cdot 10^{-5}$ $cm^2 \cdot s^{-1}$ in CH_2Cl_2 (0.35 M in $^nBu_4PF_6$). Deviations from ideality at higher sweep rates point to sluggish electron transfer kinetics as evidenced by the monotonous increase of the peak width at half height of the forward wave, E_p–$E_{p/2}$, the peak-to-peak separation, ΔE_p, and the concomitant decrease of the peak current function $i_{p,f} \cdot v^{-1/2}$ as compared to the Nernstian standard ferrocene [26]. At higher potentials a second oxidation is observed as an ill-defined, broad and chemically irreversible step at ca. +1.39 V. Similar results were obtained for **2b–d** (see Table 4).

In addition complexes **2a–d** are irreversibly reduced at rather negative potentials. Even at temperatures as low as 195 K in CH_2Cl_2 and 232 K in CH_3CN we could not observe an associated anodic return wave owing to fast chemical reactions following electron transfer. In the case of the benzonitrile complex **2d** the number of electrons transferred during this step could be determined as n = 1 by comparing the peak heights in cyclic voltammetry or the diffusional currents in chronoamperometry to those of the one-electron $Ru^{II/III}$ oxidation. For the other nitrile complexes the reduction wave is too close to the cathodic discharge limit of the electrolyte solution to allow for an accurate determination of n. Since **2a–c** display essentially the same chemistry following reduction than **2d** (*vide infra*), we propose that all of the nitrile complexes undergo a one-electron reduction process.

The product(s) generated in the chemical step following reduction of **2a** are also electroactive (ECE process)[1]. They give rise to anodic peaks at much more positive potentials which are not observed when the sweep direction is switched before reduction occurs. Thus, in CH_3CN an irreversible anodic peak is observed at –1.18 V, which itself has no cathodic counterpart. As yet, we have not been able to identify this species. In CH_2Cl_2 solution the chemical reaction takes a different course (Figures 4 a–d). When, following reduction, the sweep is returned to anodic potentials, a new and partially reversible wave is observed

[1] In the E, C nomenclature, E denotes an electron transfer and C a chemical step. The sequence of these symbols represents the sequence of the individual events in the overall process.

Table 4 Electrochemical data for complexes *cis*-$[Ru(dppm)_2Cl(NCR)]^+$ (**2a–d**) in CH_2Cl_2

R/Complex	$E_{1/2}^{+/2+}$, V	E_p^{red}, V[a]
CH_3/**2a**	+0.975	–2.23
C_2H_5/**2b**	+0.980	–2.27
^tBu/**2c**	+0.990[b]	–2.23
Ph/**2d**	+1.000	–2.14

[a] Peak potential at v = 0.1 V/s at T = 295 K.
[b] only partially reversible

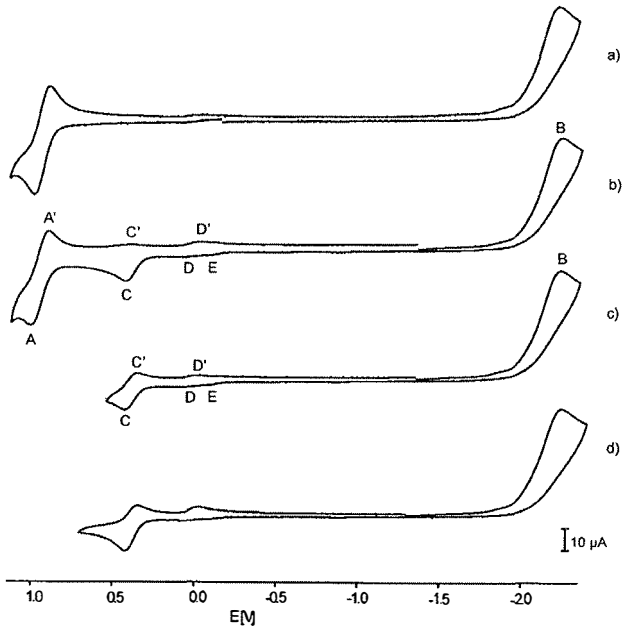


Fig. 4 CV traces of *cis*-$[Ru(dppm)_2Cl(CH_3CN)]^+$ (**2a**) in CH_2Cl_2. a) anodic scan first; b) cathodic scan first; c) potential switched past peak C; d) as in c) but after addition of small amounts of *cis*-$[Ru(dppm)_2Cl_2]$ (**1**).

at $E_{1/2}$ = +0.405 V vs. the ferrocene standard (wave C/C′ in Figures 4 b, c) along with two much smaller anodic features (D and E in Figures 4 b, c). The couple C/C′, which represents the main electrogenerated product, is only partially reversible. The associated oxidized form is therefore also chemically reactive. Indeed, if the scan is again reversed only slightly anodic of peak C, peak D′ is obtained. This feature is complementary to the small feature D already observed on the forward scan but it is now associated with distinctly larger peak currents than observed during the forward scan. At higher sweep rates this latter chemical step is suppressed and the couple C/C′ becomes chemically reversible.

The overall behavior and the half-wave potential of the C/C′ couple are highly reminiscent of *cis*-$[Ru(dppm)_2Cl_2]$ (**1**): In dichloromethane the oxidation of **1** is followed by isomerization to the more stable *trans*-isomer [4]. As shown in Figure 4 d, adding small amounts of *cis*-$[RuCl_2(dppm)_2]$ to the analyte solution causes an increase of the peak currents associated with the couple C/C′. This lets us conclude that the reduction of *cis*-$[Ru(dppm)_2Cl(CH_3CN)]^+$ in CH_2Cl_2 is followed by fast substitution of the CH_3CN ligand by chloride with the solvent as the chloride source. From the observation of small amounts of the *trans*-isomer formed in the reduction step we also conclude that CH_3CN dissociation precedes chloride addition, i.e. that the electroinduced ligand substitution is essentially a dissociative (D) process (note that in the Ru(II) oxidation state *cis*- and *trans*-$[Ru(dppm)_2Cl_2]$ do not interconvert under these conditions). Very recently *Basallote* et al. showed that nitrile substitution in cationic 18 VE complexes $[Ru(dppe)_2Cl(NCR)]^+$ also proceeds via a D mechanism [12]. The overall reduction may then be represented by Equations 1–3.

$$cis\text{-}[Ru(dppm)_2Cl(CH_3CN)]^+ + e^- \rightarrow cis\text{-}[Ru(dppm)_2Cl(CH_3CN)]^{\cdot} \quad (1)$$

$$cis\text{-}[Ru(dppm)_2Cl(CH_3CN)]^{\cdot} \rightarrow [Ru(dppm)_2Cl]^{\cdot} + CH_3CN \quad (2)$$

$$[Ru(dppm)_2Cl]^{\cdot} + CH_2Cl_2 \rightarrow cis\text{-}[Ru(dppm)_2Cl_2] + trans\text{-}[Ru(dppm)_2Cl_2] + CH_2Cl^{\cdot} \quad (3)$$

The intermediate 17 valence electron $[Ru(dppm)_2Cl]^{\cdot}$ radical is most probably of trigonal bipyramidal structure as observed for the related 16 VE cations $[Ru(L_2)_2Cl]^+$ [13 a, 27]. These are often referred to as Y-structures due to the acute equatorial L–Ru–L angle of typically ca. 80° [28]. The observed selectivity of chloride addition to this intermediate may then arise from both, the smaller steric hindrance (addition proximal to the obtuse P–Ru–Cl angle vs. addition at the P–Ru–P site) and a statistical factor (there are two possible addition sites that lead to the *cis*-isomer but only one that gives the *trans*-form).

All other complexes *cis*-$[Ru(dppm)_2Cl(NCR)]^+$ display qualitatively identical behavior as discussed for the acetonitrile complex **2a**. Relevant data are collected in Table 4. Both, the reversible oxidation potentials and, to a somewhat lesser degree, the potential of the irreversible cathodic peak are fairly insensitive to the nitrile substituent. The chemistry following reduction of **2b–d** seems somewhat more complex than for the acetonitrile complex **2a** as is evident from the appearance of weak additional peaks on the anodic reverse scan. In every case, however, reductively induced nitrile substitution by chloride constitutes the principal pathway in CH_2Cl_2 solution.

Experimental Part

NMR: Bruker AC 250, internal standard: ^1H: residual protons of the deuterated solvent indicated; ^{13}C: solvent signal; ^{31}P: H_3PO_4 (ext.). Spectra were recorded at 298 K in CD_2Cl_2 unless indicated otherwise. – IR: Elmer Paragon 1000 PC.

cis-[Ru(dppm)$_2$Cl$_2$] was prepared according to a literature method [29]. Electrochemistry was performed as detailed in an earlier publication [30].

***cis*-[Ru(dppm)$_2$Cl(NCCH$_3$)]$^+$PF$_6^-$ (2a).** To a suspension of *cis*-[Ru(dppm)$_2$Cl$_2$] (0.500 g, 0.531 mmol) and $NaPF_6$ (0.410 g, 2.22 mmol, 4 eq.) acetonitrile (15 ml, 287 mmol, 540 eq.) was added. The resulting pale yellow suspension was stirred for 2 h, filtered via a paper-tipped cannula and the solvents were removed under reduced pressure. The pale yellow powdery solid was extracted into CH_2Cl_2 (25 ml) to remove remaining $NaPF_6$ and the pale yellow solution was put to dryness *in vacuo*, affording pure **2a** as a pale yellow powder. The yields were typically in the range of 90 to 93%. Analysis calcd. for $C_{52}H_{47}ClF_6NP_5Ru$ C 57.23; H 4.34; N 1.28; found C 56.63; H 4.38; N 1.28%.

^{1}H-NMR: δ = 8.21, 7.92, 7.75, 7.65 (each m, 2H), 7.53 (m, 6H), 7.45, 7.32, 7.20, 7.08 (each m, 4H), 6.93 (m, 6H), 6.82 (dd, J = 10.7, 0.9 Hz, 1H), 6.79 (dd, J = 11.6, 1.2 Hz, 1H), 6.71 (dd, J = 11.9, 0.9 Hz, 1H), 6.68 (dd, J = 11.9, 0.9 Hz, 1H), 5.27 (m, 1H), 4.88–4.67 (m, 2H), 4.53 (dt, J = 15.55, 11.03 Hz, 1H), 1.71 (s, 3H). ^{13}C(CD_3NO_2): δ = 3.7 (CH_3CN), 41.3 (t, J = 24.2, CH_2 (dppm)), 41.7 (t, J = 40.4, CH_2 (dppm)), 125.8–134.7 (arene-C), 142.4 (CH_3CN). IR (KBr): ν = 3140 (w), 3053 (m), 3004 (w), 2988 (w), 2961 (w), 2925 (w), 1585 (m), 1573 (m), 1484 (s), 1435 (vs), 1365 (w), 1311 (w), 1261 (w), 1189 (m), 1160 (m), 1097 (s), 1026 (m), 999 (m), 840 (vs), 776 (m), 728 (vs), 696 (vs), 557 (s), 521 (s), 510 (s), 483 (s), 435 (m), 425 (m), 408 (m).

***cis*-[Ru(dppm)$_2$Cl(NCC$_2$H$_5$)]$^+$PF$_6^-$ (2b:** Method a): The synthesis was performed in analogy to the procedure for the CH_3CN complex (**2a**) with basically identical results. Method b): **2a** (0.22 g, 0.2 mmol) were dissolved in CH_2Cl_2 (20 ml) and EtCN (214 µl, 3 mmol) were added by syringe. After stirring for 2 h the pale yellow solution was dried *in vacuo*. The pale yellow solid was repeatedly washed with ether and hexanes and then dried in vacuo. Yield: 210 mg. 0.19 mmol, 95.0%. Analysis calcd. for $C_{53}H_{49}ClF_6NP_5Ru$ C 57.59; H 4.47; N 1.27; found C 56.84; H 4.44; N 1.26%.

^{1}H-NMR: δ = 8.38, 7.96, 7.76, 7.62 (each m, 2H), 7.52 (m, 6H), 7.47, 7.32, 7.22, 7.08 (each m, 4H), 6.92 (m, 6H), 6.65 (dd, J = 11.3, 0.9 Hz, 1H), 6.61 (dd, J = 11.7, 1.2 Hz, 1H), 6.56 (dd, 12.0, 0.9 Hz, 1H), 6.53 (dd, 11.9, 1.2 Hz, 1H), 5.21 (m, 1H), 4.89–4.73 (m, 2H), 4.56 (dt, J = 15.66, 10.90 Hz, 1H), 2.11 (dq, J = 16.8, 7.6 Hz, 2H), 0.81 (t, J = 7.6 Hz, 3H). ^{13}C: δ = 11.4 (CH_3), 14.8 (CH_2), 45.3 (m, CH_2), 129.5–135.9 (arene-C), 139.9 (*C*N). IR (KBr): ν = 3140 (w), 3055 (m), 2988 (w), 2925 (m), 1573 (w), 1484 (m), 1435 (s), 1365 (w), 1311 (w), 1261 (m), 1188 (m), 1159 (m), 1096 (s), 1026 (m), 999 (m), 836 (vs), 776 (m), 731(s), 727 (s), 699 (s), 557 (s), 543 (m), 521 (s), 511 (s), 483 (s), 435 (m), 413 (m).

***cis*-[Ru(dppm)$_2$Cl(NC^{t}Bu)]$^+$PF$_6^-$ (2c): 2a** (0.220 g, 0.2 mmol) were dissolved in CH_2Cl_2 (20 ml) and ^{t}BuCN (220 µl, 2.0 mmol, 10 eq.) were added by syringe. After stirring for 2 h under ambient conditions the pale yellow solution was filtered and dried under reduced pressure. The pale yellow solid was repeatedly washed with ether and hexanes and then dried in vacuo. Yield: 200 mg, 0.177 mmol, 89.0%. Analysis calcd. for $C_{55}H_{53}ClF_6NP_5Ru$ C 59.01; H 4.77; N 1.25; found C 58.15; H 4.80; N 1.25%.

^{1}H-NMR: δ = 8.50, 8.23 (each m, 2H), 8.07 (dd, J = 10.1, 3.6 Hz, 1H), 8.06 (dd, J = 10.1, 2.2 Hz, 1H), 7.93 (m, 2H), 7.73 (m, 6H), 7.60 (m, 8H), 7.41 (m, 6H), 7.20–7.04 (m, 8H), 6.86 (m, 4H), 5.56 (m, 1H), 5.28 (m, 1H), 5.07 (dt, J = 15.56, 11.8 Hz, 1H), 4.84 (dt, J = 16.24, 10.90 Hz, 1H), 1.17 (s, 9H). ^{13}C-NMR (CD_3NO_2): δ = 26.2 (CH_3), 29.9 (CCH_3), 41.8, 42.2 (m, CH_2), 126.9–132.6 (arene-C), 141.5 (*C*N). IR (KBr): ν = 3140 (w), 3052 (m), 2979 (w), 2933 (w), 2869 (w), 1951 (vw), 1899 (vw), 1586 (w), 1572 (w), 1485 (m), 1476 (w), 1435 (s), 1399 (w), 1384 (w), 1370 (w), 1314 (w), 1235 (w), 1189 (w), 1159 (w), 1098 (s), 1026 (m), 999 (m), 836 (vs), 772 (m), 729 (s), 723 (s), 695 (s), 557 (s), 545 (m), 521 (s), 510 (s), 483 (s), 434 (m), 415 (m).

***cis*-[Ru(dppm)$_2$Cl(NCPh)]$^+$SbF$_6^-$ (2d):** 0.300 g (0.319 mmol) of **1** were dissolved in CH_2Cl_2 (40 ml) and solid $NaSbF_6$ (0.330 g, 1.27 mmol, 4 eq.) and PhCN (17.6 ml, 17.76 g, 172 mmol, 540 eq.) were added. The solution was stirred for 2 h at room temperature. The solvents were then removed under reduced pressure and the crude product was washed with Et_2O (2 · 20 ml). The yellow solid thus obtained was extracted into CH_2Cl_2, filtered and the solvent removed in vacuo. The yellow residue was then recrystallized from $CH_3NO_2/C_2H_4Cl_2$ to give yellow diamond shaped crystals of **2d**. Yield: 0.246 g, 62.0%. Analysis calcd. for $C_{57}H_{49}ClF_6NP_4RuSb$ C 55.03; H 3.97; N 1.13; found C 54.15; H 3.88; N 1.12%.

^{1}H-NMR: δ = 8.31 (m, 2H), 8.00 (dd, J = 10.1, 1.6 Hz, 1H), 7.95 (dd, J = 10.3, 1.6 Hz, 1H), 7.86 (m, 3H), 7.71–7.62 (m, 4H), 7.50–7.39 (m, 13H), 7.34–7.18 (m, 6H), 7.11–7.06 (m, 5H), 6.98–6.91 (m, 7H), 6.71 (dd, J = 11.0, 0.7 Hz, 1H), 6.67 (dd, J = 10.3, 1.15 Hz, 1H), 6.60 (dd, 11.7, 0.9 Hz, 1H), 6.56 (dd, 11.9, 1.15 Hz, 1H), 5.26 (m, 1H), 4.95–4.79 (m, 2H), 4.65 (dt, J = 15.83, 11.01 Hz, 1H). IR (KBr): ν = 3142 (w), 3050 (m), 3025 (w), 3003, (w), 2986 (w), 2869 (w), 2962 (w), 1586 (w), 1571 (w), 1483 (m), 1447 (w), 1434 (s), 1358 (w), 1333 (w), 1311 (w), 1263 (w), 1188 (w), 1178 (w), 1159 (w), 1096 (s), 1025 (m), 998 (m), 752 (m), 728 (s), 695 (s), 656 (s), 615 (m), 544 (m), 520 (s), 508 (s), 480 (s), 436 (m), 415 (m) 381 (m), 288 (s).

***cis*-[Ru(dppm)$_2$Cl(Py)]$^+$SbF$_6^-$ (3a):** 0.105 g (0.111 mmol) of **2a** (SbF_6^- salt), dissolved in CH_2Cl_2 (10 ml) were treated with pyridine (110 µl, 0.112 g, 1.42 mmol). A pale yellow precipitate gradually formed. After 2 h, the solution was filtered and the remaining solid washed with ether and hexanes and dried *in vacuo*. Yield: 0.108 g. Analysis calcd. for $C_{55}H_{49}ClF_6NP_4RuSb$ C 54.14; H 4.05; N 1.15; found C 53.70; H 4.08; N 1.13%. This compound is very poorly soluble in all common organic solvents and was found to be impure owing to its tendency to dismutation into *cis*-[Ru(dppm)$_2$Cl$_2$] (**1**) and *cis*-[Ru(dppm)$_2$(Py)$_2$]$^{2+}$ (^{31}P: δ = 3.2, –18.9, each t, J = 21.4 Hz) in polar organic solvents.

***cis*-[Ru(dppm)$_2$Cl(4-DMAP)]$^+$PF$_6^-$ (3b):** Method a): *cis*-[Ru(dppm)$_2$Cl$_2$] (0.160 g, 0.17 mmol), 4-DMAP (0.042 g, 0.34 mmol) and KPF_6 (0.125 g, 0.68 mmol) were suspended in acetone and stirred for 12 h at room temperature. The yellow solution was filtered from the white precipitate and the solvent removed *in vacuo*. The resulting yellow solid was extracted into $CHCl_3$ (15 ml) and filtered to remove remaining KPF_6. The solution was concentrated *in vacuo*. Cold ethanol (5 ml) precipitated a pale yellow powder which was collected and dried. Yield: 0.158 g, 79.3%. By ^{31}P-NMR spectroscopy, this solid was identified as a mixture of **3b** (93%), *cis*-[Ru(dppm)$_2$(4-DMAP)$_2$]$^{2+}$ (3%, ^{31}P: δ = 10.7, –9.3, each t, J = 39.2 Hz) and trans-[Ru(dppm)$_2$Cl$_2$] (4%). Attempts to further purify **3b** from $CHCl_3$/EtOH led to dismutation.

Method b): 0.08 g of **2a** (73 µmol) and 4-DMAP (0.027 g, 221 µmol) were dissolved in CH_2Cl_2 (15 ml) and stirred for 10 h under ambient conditions. The solvent was removed in vacuo and the intense yellow solid that remained was washed with Et_2O (3 · 10 ml) and then dried *in vacuo*. Yield: 0.078 g, 66.5 µmol, 90.8%. Analysis calcd. for $C_{57}H_{54}ClF_6N_2P_5Ru$ C 58.39; H 4.64; N 2.39; found C 57.20; H 4.59; N 2.39%.

^{1}H-NMR (Acetone-d_6): δ = 8.31 (m, 2H), 8.05 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.77, 7.68, 7.57 (each m, 2H), 7.52–7.42 (m, 6H), 7.39–7.28 (m, 6H), 7.22 (m, 5H), 7.13 (m, 8H), 7.03 (m, 2H), 6.98 (dd, J = 7.32, 2.45 Hz, 1H), 6.94 (dd, J = 7.00, 2.44 Hz, 1H), 6.91 (dd, J = 7.63,

2.44 Hz, 1 H), 6.86 (d(br.), J = 11.3 Hz), 6.80 (dd, J = 11.21, 1.43 Hz, 1 H), 6.75 (dd, J = 11.68, 0.91 Hz, 1 H), 6.71 (dd, J = 11.04, 1.22 Hz, 1 H), 5.88 (ddd, J = 16.1, 10.0, 9.8 Hz, 1 H, CH_2(dppm)), 5.78 (d, J = 7.18 Hz, 2 H, arene H (4-DMAP), 4.96 (d, J = 11.04 Hz, 1 H), 4.92 (d, J = 8.73 Hz, 1 H), 4.75 (dt, J = 15.85, 10.8 Hz, 1 H), 2.87 (s, 6 H). ^{13}C (CD_3NO_2): δ = 38.8 (NCH_3), 40.8, 43.6 (m, CH_2), 106.1 (s, *ortho*-C (4-DMAP)), 128.2–135.1 (arene-C), 136.2, 136.6 (*ipso*-C (dppm)), 154.5 (*ipso*-C(4-DMAP)), 156.6 (t, J_{NC} = 1.85, *para*-C (DMAP). IR (KBr): ν = 3140 (w), 3052 (m), 2976 (w), 2922 (w), 2849 (w), 1622 (s), 1572 (w), 1537 (m), 1533 (m), 1484 (m), 1435 (s), 1389 (m), 1307 (w), 1230 (m), 1188 (w), 1159 (w), 1095 (s), 1063 (w), 1026 (w), 1013 (m), 999 (m), 987 (m), 987 (w), 950 (w), 839 (vs), 806 (m), 770 (m), 725 (s), 696 (s), 557 (s), 542 (m), 514 (s), 510 (s), 483 (s), 433 (m), 414 (m).

***cis*-[Ru(dppm)$_2$Cl(NMe(SiMe$_3$)$_2$)]$^+$PF$_6^-$ (4):** 0.200 g (0.183 mmol) of **2a**, dissolved in CH_2Cl_2 were treated with $NMe(SiMe_3)_2$ (600 µl, 0.478 g, 2.7 mmol). The resulting solution was stirred at 40 °C for 2 h, then filtered and dried *in vacuo*. The yellow solid thus obtained was repeatedly washed with ether and hexanes to give **4**. Yield: 0.207 g, 92.3%. Analysis calcd. for $C_{57}H_{65}ClF_6NP_5RuSi_2$ C 55.85; H 5.34; N 1.14; found C 54.48; H 5.13; N 1.15%.

^{1}H-NMR: δ = 8.06 (m, 1 H), 7.90 (m, 2 H), 7.70 (m, 1 H), 7.68–7.53 (m, 8 H), 7.45–7.18 (m, 14 H), 7.11 (m, 6 H), 7.01 (m, 2 H), 6.91 (dd, J = 7.93, 2.34 Hz, 1 H), 6.85 (dd, J = 7.63, 2.34 Hz, 1 H), 6.74 (dd, J = 11.29, 1.22 Hz, 1 H), 6.71 (dd, J = 11.29, 1.22 Hz, 1 H), 6.49 (dd, J = 11.90, 0.92 Hz, 1 H), 6.46 (dd, J = 11.90, 1.22 Hz, 1 H), 5.37 (m, 1 H), 4.74 (dd, J = 10.83, 7.78 Hz, 2 H), 4.58 (m, 1 H), 2.05 (s, 3 H), 0.07, J(^{29}Si) = 3.38 Hz). ^{13}C: δ = 1.93 ($SiCH_3$), 35.9 (*C*N), 44.8, 45.2 (m, CH_2), 127.9–134.1 (arene-C). IR (KBr): ν = 3140 (w), 3053 (m), 2979 (w), 2952 (w), 2920 (w), 2850 (w), 1572 (w), 1484 (m), 1435 (s), 1358 (w), 1311 (w), 1260 (m), 1189 (w), 1157 (w), 1096 (s), 1026 (m), 998 (m), 950 (w), 839 (vs), 728 (s), 696 (s), 557 (s), 542 (m), 519 (s), 510 (s), 483 (s), 437 (m), 413 (m).

***cis*-[Ru(dppm)$_2$Cl(CN^{t}Bu)]$^+$PF$_6^-$ (*cis*-5):** 0.180 g (0.165 mmol) of **2a** were dissolved in CH_2Cl_2 (15 ml). The solution was immersed into an ice-bath and, after 25 min, ^{t}BuNC (180 µl, 0.132 g, 1.59 mmol) were added by syringe. The solution turned colourless almost immediately. After allowing to stir for 30 min the solvent was driven off *in vacuo* and the resulting, almost colourless solid was washed with ether and hexanes. After drying in vacuo at +4° C 0.182 g (97.5%) ***cis*-5** was obtained in 98.8% isomeric purity as a very pale yellow, powdery solid. In solution, ***cis*-5** slowly converts to its *trans*-isomer. After slow evaporation of a concentrated solution of the original product in acetone/toluene pure ***trans*-5** was obtained in quantitative yield as transparent, very pale orange plates. ***cis*-5**: Analysis calcd. for $C_{57}H_{53}ClF_6NP_5Ru$ C 59.01; H 4.77; N 1.75; found C 58.64; H 4.75; N 1.73%.

^{1}H-NMR: δ = 8.30 (dd, J = 11.29, 2.14 Hz, 1 H), 8.26 (dd, J = 11.29, 2.14 Hz, 1 H), 7.95–7.81 (m, 4 H), 7.63 (m, 2 H), 7.50 (m, 6 H), 7.40 (m, 4 H), 7.32 (m, 4 H), 7.20 (m, 6 H), 6.96 (m, 8 H), 6.69 (dd, J = 10.0, 0.92 Hz, 1 H), 6.66 (dd, J = 11.29, 1.22 Hz, 1 H), 6.58 (dd, J = 11.60, 0.92 Hz, 1 H), 6.54 (dd, J = 11.90, 1.22 Hz, 1 H), 5.15 (m, 1 H), 4.96–4.84 (m, 2 H), 4.70 (dt, J = 15.87, 11.0 Hz, 1 H), 1.14 (s, 9 H). ^{13}C-NMR: δ = 27.3 (CCH_3), 29.5 (CCH_3), 43.8, 44.8 (m, CH_2), 127.6–137.8 (arene-C). IR (KBr): ν = 3144 (w), 3052 (m), 2981 (w), 2926 (w), 2871 (w), 2851 (w), 2157 (s), 1616 (w), 1585 (w), 1484 (m), 1435 (s), 1398 (w), 1370 (m), 1311 (w), 1276 (w), 1233 (m), 1200 (m), 1190 (m), 1159 (w), 1098 (s), 1026 (m), 999 (m), 838 (vs), 767 (w), 728 (s), 695 (s), 670 (m), 616 (w), 557 (s), 541 (w), 519 (s), 509 (s), 481 (m), 441 (m), 379 (w).

***trans*-5:** Analysis calcd. for $C_{57}H_{53}ClF_6NP_5Ru$ C 59.01; H 4.77; N 1.75; found C 57.24; H 4.76; N 1.76%.

^{1}H-NMR (CD_3NO_2) δ = 7.76 (m, 8 H), 7.64 (m, 8 H), 7.54 (m, 8 H), 7.39 (t, J = 7.54 Hz, 8 H), 5.41 (dqui, J = 15.6, 4.9 Hz, 2 H), 5.23 (dqui, J = 15.6, 4.2 Hz), 0.53 (s, 9 H). ^{13}C-NMR (CD_3NO_2): δ = 30.0 (s,CH_3), 30.8 (s, CCH_3), 48.4 (qui, J = 12.1 Hz), 129.6 (qui, J = 2.63 Hz), 130.3 (qui, J = 2.50 Hz), 130.6 (qui, J = 2.50 Hz), 132.08 (s), 132.80 (s), 130.0 (qui, J = 12.37 Hz), 133.9 (qui, J = 3.16 Hz), 134.7 (qui, J = 2.90 Hz), 135.02 (qui, J = 11.58 Hz), 143.08 (s, *C*N). ^{31}P (CD_3NO_2): --8.9 (s). IR (KBr): ν = 3140 (w), 3055 (m), 3023 (w), 2972 (w), 2927 (w), 2127 (s), 1484 (m), 1435 (s), 1368 (w), 1307 (w), 1231 (m), 1190 (m), 1098 (s), 1024 (m), 998 (m), 839 (vs), 739 (s), 726 (s), 713 (m), 694 (s), 557 (s), 518 (s), 505 (s), 483 (s).

***cis*-[Ru(dppm)$_2$(CH$_3$CN)$_2$]$^{2+}$(BF$_4^-$)$_2$ (6):** *cis*-[Ru(dppm)$_2$Cl$_2$] (0.300 g, 0.319 mmol) and $AgBF_4$ (0.137 g, 0.702 mmol, 2.2 eq.) were suspended in 15 ml of CH_3NO_2 to which CH_3CN (25 µl, 4.8 mmol, 15 eq.) had been added. After stirring for 30 min at room temperature, the resulting greyish-white solid (AgCl and remaining $AgBF_4$) was allowed to settle and the colourless solution was transferred by filter cannula into a Schlenk flask. The solvents were condensed off *in vacuo*. The remaining white solid was extracted into dichloromethane (15 ml), filtered again and dried in vacuo to afford pure **6** as a white powder. **6** could be crystallized by slow evaporation of a solution in CH_3NO_2/CH_2Cl_2 to afford colourless square plates. Analysis calcd. for $C_{54}H_{50}B_2F_8N_2P_4Ru$ C 57.65; H 4.48; N 2.49; found C 57.18; H 4.44; N 2.46%.

^{1}H-NMR (CD_3NO_2): δ = 8.04 (m, 8 H), 7.75 (m, 12 H), 7.51 (m, 4 H), 7.42 (tt, J = 7.95, 1.30 Hz, 4 H), 7.31 (m, 4 H), 7.24 (t(br.), J = 7.20 Hz, 4 H), 6.87 (m, 4 H), 5.57 (m, 2 H), 4.89 (m, 2 H), 2.16 (s, 6 H). ^{31}P-NMR (CD_3NO_2): δ = –6.03, –20.65 (each t, J = 17.1 Hz). ^{13}C-NMR (CD_3NO_2): δ = 3.76 (s, CH_3), 40.86 (quint, J = 28.85 Hz, CH_2(dppm)), 130.1 (t, J = 5.22 Hz), 130.71 (tt, J = 19.8, 4.95 Hz), 130.9 (t, J = 5.40 Hz), 131.0 (t, J = 5.35 Hz), 131.39 (t, J = 5.24 Hz), 131.42 (t, J = 5.33 Hz), 132.3 (t, J = 6.62 Hz), 132.6 (s), 132.9 (t, J = 6.29 Hz), 132.92 (t, J = 6.60 Hz), 133.0 (s), 133.6 (s), 136.0 (tt, J = 19.80, 4.95 Hz). IR (KBr): ν = 3136 (w), 3052 (m), 3020 (w), 2988 (w), 2961 (w), 2930 (w), 2319 (w), 2287 (w), 1585 (w), 1573 (w), 1540 (w), 1483 (w), 1435 (w), 1372 (w), 1313 (w), 1283 (w), 1261 (w), 1188 (w), 1098 (vs), 1072 (vs), 1060 (vs), 1050 (vs), 998 (m), 843 (w), 802 (w), 730 (s), 723 (s), 697 (s), 544 (m), 517 (s), 510 (s), 485 (s), 441 (m), 425 (m).

X-ray analyses: Diamond shaped, yellow single crystals of **2a, b** were grown from CH_3NO_2/$C_2H_4Cl_2$. ***trans*-5a** crystallized from acetone/toluene as pale orange plates which contained one molecule of acetone per unit cell. Single crystals were mounted onto glass fibers with high viscosity oil. Data collection was performed at 173(2) K on a Siemens P4 diffractometer. Structure solution was performed by direct methods using the SHELXTL 5.1 package. Structures were refined versus F^2. In **2a**, the PF_6^- counterions are disordered about the F5–P–F6 axis with occupancy factors of 69% and 31% for the two alternative sets of equatorial positions. In **2b**, the methyl group of the propionitrile ligand and four of the P-atoms are disordered over two positions and the respective occupancies were freely refined. The PF_6^- counterions of **trans-5**, the ^{t}Bu-substituent on the nitrile and the solvent molecule are all disordered. Details of the X-ray structure determinations have been deposited at the Cambridge Crystallographic Data Centre, as CCDC 138525 (**2a**), CCDC 138526 (**2b**) and CCDC 138627 (*trans*-**5**). Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-12 23-3 36-0 33; e-mail deposit@ccdc.cam.ac.uk or http: //www.ccdc.cam.ac.uk).

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