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Acetonitrile and propionitrile exchange at palladium(II) and platinum(II) †

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Ligand exchange at square-planar $[Pd(MeCN)_4]^{2+}$ and $[Pd(EtCN)_4]^{2+}$ has been studied by ^1H NMR line broadening and at $[Pt(MeCN)_4]^{2+}$ and $[Pt(EtCN)_4]^{2+}$ by isotopic labelling using ^1H NMR spectroscopy in deuteriated nitromethane. Exchange takes place *via* two-term rate laws $R_{ex}/4 = (k_1 + k_2[RCN])c_M$ with well defined k_1 paths. Rate constants per co-ordination site k_1^{298}/s^{-1}, $k_2^{298}/kg\ mol^{-1}\ s^{-1}$ are 6.9 ± 1.6, 34 ± 3; 0.59 ± 0.12, 34 ± 3; 10.7 ± 1.8, 35 ± 4; $(5.1 \pm 2.3) \times 10^{-6}$, $(2.8 \pm 0.2) \times 10^{-5}$ and $(5.5 \pm 1.0) \times 10^{-6}$, $(3.3 \pm 0.2) \times 10^{-5}$ for $[Pd(MeCN)_4][CF_3SO_3]_2$, $[Pd(MeCN)_4][BF_4]_2$, $[Pd(EtCN)_4][CF_3SO_3]_2$, $[Pt(MeCN)_4][CF_3SO_3]_2$ and $[Pt(EtCN)_4][CF_3SO_3]_2$, respectively. For $[Pd(MeCN)_4]^{2+}$ the k_1 path is much larger for triflate than for tetrafluoroborate as counter ion. Changing the tetrafluoroborate concentration has no effect on the exchange rate of acetonitrile at $[Pd(MeCN)_4]^{2+}$. In this case the k_1 path is ascribed to an attack by solvent at the metal centre. For triflate saturation kinetics is observed. This can be rationalized in terms of ion-pair formation followed by reversible intramolecular exchange of nitrile for triflate within the ion pair, with an equilibrium constant $K_{ip}^{300} = 8 \pm 2$ kg mol^{-1} and a rate constant $k^{300} = 12.5 \pm 1.3\ s^{-1}$. All activation entropies are negative, indicating associative activation. A new, simple one-step synthesis of the substrate complexes as their triflate salts, using $[M(acac)_2]$ (acac = acetylacetonate) as starting material, and of $[Pd(MeCN)_4][BF_4]_2$ using palladium(II) acetate, is described.

Exchange of oxygen-, nitrogen-, sulfur- and carbon-donor ligands at square-planar homoleptic palladium(II) and platinum(II) complexes has been studied.[1–8] Recent synthesis of the homoleptic platinum(II) propionitrile complex[9] prompted us to investigate its solvent exchange in nitromethane diluent, since no exchange of N-bonded ligands at platinum(II) has been studied so far. In nitromethane solvent with triflate ($CF_3SO_3^-$) as counter ion, this reaction unexpectedly displayed a two-term rate law with a well defined nitrile-independent pathway. This is in contrast to acetonitrile exchange at $[Pd(MeCN)_4]^{2+}$ in tetrafluoroborate-containing nitromethane, which has been reported to proceed *via* a simple direct exchange mechanism.[8] The nitrile-independent pathway observed in our case could be due to a nitromethane solvent path and/or an ion-pairing mechanism with triflate similar to that described previously by Alibrandi *et al.*[10] and Yagyu *et al.*[11] Further to test the occurrence of two-term rate laws for nitrile exchange in nitromethane solvent, we have also studied exchange at $[Pd(EtCN)_4]^{2+}$ and $[Pt(MeCN)_4]^{2+}$ in triflate-containing solutions, and have reinvestigated the acetonitrile exchange at $[Pd(MeCN)_4]^{2+}$ in nitromethane media containing various concentrations of triflate and tetrafluoroborate. In this context we also report a new method of synthesis of $[M(RCN)_4]^{2+}$ (M = Pd or Pt, R = Me or Et) as their triflate salts and for the tetrafluoroborate salt of $[Pd(MeCN)_4]^{2+}$.

Experimental

General procedures and chemicals

Acetonitrile (Labscan AR or Merck Lichrosolv), propionitrile (Merck zS or Janssen Chimica 99%+), diethyl ether (Labscan AR), [$^2H_3$]nitromethane (Janssen Chimica 99%) and [$^2H_3$]-acetonitrile (Glaser AG 99%) were dried with and stored over 4 Å activated molecular sieves. Palladium(II) acetate (Acros), trifluoromethanesulfonic acid (Merck zS), tetrafluoroboric acid [Aldrich 54% (w/w) solution in Et_2O], [$^2H_5$]bromoethane (Larodan 98%) and tetra-*n*-butylammonium trifluoromethanesulfonate (Lancaster 99%) were used as received. Metal complexes were prepared under nitrogen using standard Schlenk techniques; $[Pd(acac)_2]$, $[Pt(acac)_2]$ (acac = acetylacetonate), NEt_4CN and NEt_4BF_4 were prepared according to the literature.[12–14] The solvento compounds $[Pd(MeCN)_4][CF_3SO_3]_2$ **1**, $[Pd(EtCN)_4][CF_3SO_3]_2$ **2**, $[Pt(MeCN)_4][CF_3SO_3]_2$ **3**, $[Pt(EtCN)_4][CF_3SO_3]_2$ **4** and $[Pd(MeCN)_4][BF_4]_2$ **5** were prepared according to equation (1), where M = Pd or Pt, L = acetylacetonate or acetate and $A = CF_3SO_3$ or BF_4. This method is straightforward and simple, eliminating the use of halide abstraction or oxidation of Pd^0 as described previously.[9,15] The acetylacetonato and acetato complexes are commercially available or easily prepared and can be stored without decomposition. Compounds **1**, **2** and **5** are very sensitive to moisture and must be handled under dry nitrogen. The somewhat too low nitrogen values in their elemental analyses can be explained by partial decomposition during transportation. Compounds **3** and **4** are much less sensitive to moisture but have to be stored in closed vessels. Elemental analyses were by Mikro Kemi AB, Uppsala, Sweden. Infrared spectra were recorded on a Nicolet 20 SXC FT-IR spectrometer as Nujol mulls between NaCl windows or in the case of C_2D_5CN on a Bio-Rad FTS 6000 spectrometer in the liquid phase between NaCl windows.

$$ML_2 + 4\ RCN \xrightarrow[-HL]{HA} [M(RCN)_4]^{2+} \qquad (1)$$

Preparations

$[Pd(MeCN)_4][CF_3SO_3]_2$ 1. The compound $[Pd(acac)_2]$ (0.334 g, 1.096 mmol) was suspended in MeCN (*ca.* 6 cm^3) in a Schlenk tube, CF_3SO_3H (0.75 cm^3) was added to the stirred suspension and stirring was continued at room temperature for 22 h. The now clear solution was reduced to half of its volume by evaporation and diethyl ether (35 cm^3) was added dropwise. The sealed tube was put in a freezer overnight and the light yellow solid formed was collected by Schlenk filtration, washed twice with ether and dried *in vacuo*. The yield was 0.573 g (92%) (Found: C, 20.8; H, 2.2; N, 9.2. Calc. for $C_{10}H_{12}F_6N_4O_6PdS_2$: C, 21.1; H, 2.1; N, 9.9%). ^1H NMR (CD_3NO_2, 8 °C): δ 2.66 (s). IR (cm^{-1}): 2351 [ν(C–N)].

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† Supplementary data available (No. SUP 57305, 4 pp.): inverse lifetimes and exchange rates. See *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

[Pd(EtCN)$_4$][CF$_3$SO$_3$]$_2$ 2. Compound **2** was prepared similarly to **1** from [Pd(acac)$_2$] and EtCN giving a yellow solid in 70% yield (Found: C, 26.9; H, 3.4; N, 8.1. Calc. for $C_{14}H_{20}F_6N_4O_6PdS_2$: C, 26.9; H, 3.2; N, 9.0%). ^{1}H NMR (CD$_3$NO$_2$, −20 °C): δ 1.35 (t, $J = 7.52$ Hz) and 3.00 (q). IR (cm^{-1}): 2331 [ν(C–N)].

[Pt(MeCN)$_4$][CF$_3$SO$_3$]$_2$ 3. Compound **3** was prepared similarly to **1** from [Pt(acac)$_2$] and MeCN with prolonged reaction time (48 h) giving a white solid in almost quantitative yield (Found: C, 18.4; H, 1.8; N, 8.4. Calc. for $C_{10}H_{12}F_6N_4O_6PtS_2$: C, 18.3; H, 1.8; N, 8.5%). ^{1}H NMR (CD$_3$NO$_2$): δ 2.83 (s). IR (cm^{-1}): 2353 [ν(C–N)].

[Pt(EtCN)$_4$][CF$_3$SO$_3$]$_2$ 4. Compound **4** was prepared similarly to **3** from [Pt(acac)$_2$] and EtCN giving a precipitate which was redissolved in EtCN and reprecipitated with ether yielding a slightly off-white solid in 83% yield (Found: C, 23.4; H, 2.9; N, 7.7. Calc. for $C_{14}H_{20}F_6N_4O_6PtS_2$: C, 23.6; H, 2.8; N, 7.9%). ^{1}H NMR (CD$_3$NO$_2$): δ 1.41 (t, $J = 7.52$ Hz) and 3.17 (q). IR (cm^{-1}): 2334 [ν(C–N)]. It was also prepared according to Kukushkin *et al.*[9]

[Pd(MeCN)$_4$][BF$_4$]$_2$ 5. Compound **5** was prepared similarly to **1** from Pd(O$_2$CMe)$_2$ and MeCN giving a yellow solid in almost quantitative yield (Found: C, 21.2; H, 2.8; N, 11.9. Calc. for $C_8H_{12}B_2F_8N_4Pd$: C, 21.6; H, 2.7; N, 12.6%). ^{1}H NMR (CD$_3$NO$_2$): δ 2.66 (s). IR (cm^{-1}): 2355 [ν(C–N)].

CD$_3$CD$_2$CN. Deuteriated propionitrile was prepared from C$_2$D$_5$Br and NEt$_4$CN using the method of Kobler *et al.*[16] Two distillations gave a clear liquid in 42% yield. B.p. = 91–95 °C (760 mmHg, *ca.* 10^5 Pa). ^{13}C NMR (CDCl$_3$): δ 8.75 (spt, $^1J_{CD} = 19.8$), 9.33 (qnt, $^1J_{CD} = 20.9$ Hz) and 120.6 (s). IR (cm^{-1}): 2243 [ν(C–N)].

NMR measurements

Reaction (2) was studied by use of NMR line broadening for

$$[M(RCN)_4]^{2+} + n\,RCN^* \rightleftharpoons [M(RCN)_{4-n}(RCN^*)_n]^{2+} + n\,RCN \quad (2)$$

the palladium compounds **1**, **2** and **5** and isotopic labelling for those of platinum, **3** and **4**. The NMR spectra were recorded on a Varian UNITY 300 spectrometer working at 299.79 (^{1}H) or 75.39 (^{13}C) MHz. The temperature was measured either with a platinum resistor or using the temperature-dependent shifts of the CH$_2$ and OH protons of ethylene glycol. The value of T_1 was determined for free MeCN and EtCN using the inversion-recovery technique. Chemical shifts are given in ppm downfield from SiMe$_4$ using CD$_2$HNO$_2$ (^{1}H NMR δ 4.33) or CDCl$_3$ (^{13}C NMR δ 77.0) as internal standard. Samples for line broadening experiments were prepared in a glove-box by weighing the palladium complexes and NBu$^n_4$CF$_3$SO$_3$ or NEt$_4$BF$_4$ in an NMR tube, adding CD$_3$NO$_2$ (0.800 cm^3), CH$_2$Cl$_2$ (0.020 cm^3) and the nitrile (0.010–0.080 cm^3) and sealing the tube. Spectra were collected as 16–64 repetitions using 90° pulses and (3–5) T_1 between pulses. The value of T_2^* was determined from the CH$_2$Cl$_2$ peak, which was shown to be approximately 0.05 Hz narrower than the nitrile peaks in the absence of exchange. Coupling constants and the temperature dependence of the resonance frequencies were determined in the slow-exchange region (−20 to 10 °C). Samples for isotopic labelling experiments were prepared by weighing the platinum complexes in an NMR tube, adding CD$_3$NO$_2$ (0.800 cm^3) and allowing the sample to temperature equilibrate in the probe. Reaction was started by adding the deuteriated ligand (0.015–0.080 cm^3). Spectra were collected at equal intervals of time until the reaction was at least 90% complete using 90° pulses and one to four repetitions with 5T_1 between pulses. Peak areas were determined from peak heights and widths (in the case of **3**) or as the sum of the integrals of CH$_3$ and CH$_2$ protons (in the case of **4**). The overall error in the observed rate constants was *ca.* 15% in the line broadening experiments and only *ca.* 2% in the isotopic labelling experiments.

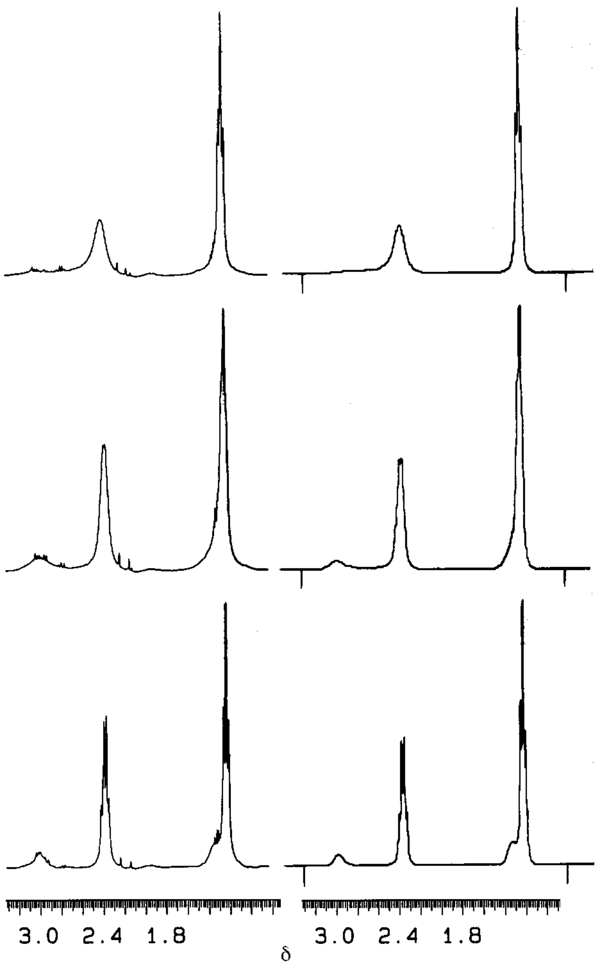


Fig. 1 Experimental (left) and calculated (right) ^{1}H NMR spectra of [Pd(EtCN)$_4$]$^{2+}$ **2** and free EtCN. $c_M = 57.2$ mmol kg^{-1}, [L] = 1.031 mol kg^{-1}, $T = 301.5$ K, $T_2^* = 0.6$ s, $\tau_C^{-1} = 63.1$ s^{-1} (bottom); $T = 316.3$ K, $T_2^* = 0.5$ s, $\tau_C^{-1} = 135$ s^{-1} (middle); $T = 336.4$ K, $T_2^* = 0.7$ s, $\tau_C^{-1} = 271$ s^{-1} (top)

Results and Discussion

Palladium complexes

Proton NMR spectra of the palladium complexes **1**, **2** and **5** and the corresponding free nitrile show peaks with different shifts for the two types of ligands. At room temperature the peaks are broadened due to exchange. Mean lifetimes of free nitrile, τ_F, were determined by visual comparison of the experimental spectra with spectra simulated by the computer program DNMR 5,[17] see Fig. 1. The inverse of the mean lifetime of a particular co-ordinated nitrile, τ_C^{-1}, was calculated from equation (3), where c_M and [L] denote concentrations of

$$R_{ex} = 4\,c_M\tau_C^{-1} = [L]\tau_F^{-1} \quad (3)$$

metal complex and free nitrile, respectively and R_{ex} is the total rate of exchange (Table S1, SUP 57305). Assuming a first-order dependence on complex concentration, a plot of τ_C^{-1} *versus* [L] should be linear. Fig. 2 shows such plots for **1**, **2** and **5**, respectively, validating the rate law (4), where k_1 and k_2 denote rate constants for exchange per co-ordination site.

$$R_{ex} = (k_1 + k_2[L])\,4c_M \quad (4)$$

Table 1 Activation parameters and rate constants for reaction (2)[a]

Complex (T range/K)	k_1^{298b}/s^{-1}	k_2^{298b}/kg mol^{-1}	$\Delta H_1^‡$/kJ mol^{-1}	$\Delta H_2^‡$/kJ mol^{-1}	$\Delta S_1^‡$/J K^{-1} mol^{-1}	$\Delta S_2^‡$/J K^{-1} mol^{-1}
1 $[Pd(MeCN)_4{}^{2+}]$ (297–338)	6.9 ± 1.6[c]	34 ± 3	64.7 ± 0.7[c]	48.3 ± 1.6	−12 ± 2[c]	−53 ± 5
2 $[Pd(EtCN)_4]^{2+}$ (301–337)	10.7 ± 1.8[c]	35 ± 4	59 ± 6[c]	42 ± 4	−28 ± 18[c]	−74 ± 13
3 $[Pt(MeCN)_4]^{2+}$ (296–335)	(5.1 ± 2.3) × 10^{-6}	(2.8 ± 0.2) × 10^{-5}	83 ± 8	89 ± 5	−66 ± 25	−35 ± 15
4 $[Pt(EtCN)_4]^{2+}$ (303–334)	(5.5 ± 1.0) × 10^{-6}	(3.3 ± 0.2) × 10^{-5}	97 ± 3	77.8 ± 1.1	−21 ± 8	−70 ± 4
5 $[Pd(MeCN)_4]^{2+}$ (300–338)	0.59 ± 0.12	34 ± 3	55 ± 4	44.8 ± 1.5	−65 ± 12	−65 ± 5

[a] Quoted errors are estimated from the standard deviations of the rate constants at all temperatures. [b] Calculated from the temperature dependence. [c] Composite quantity.

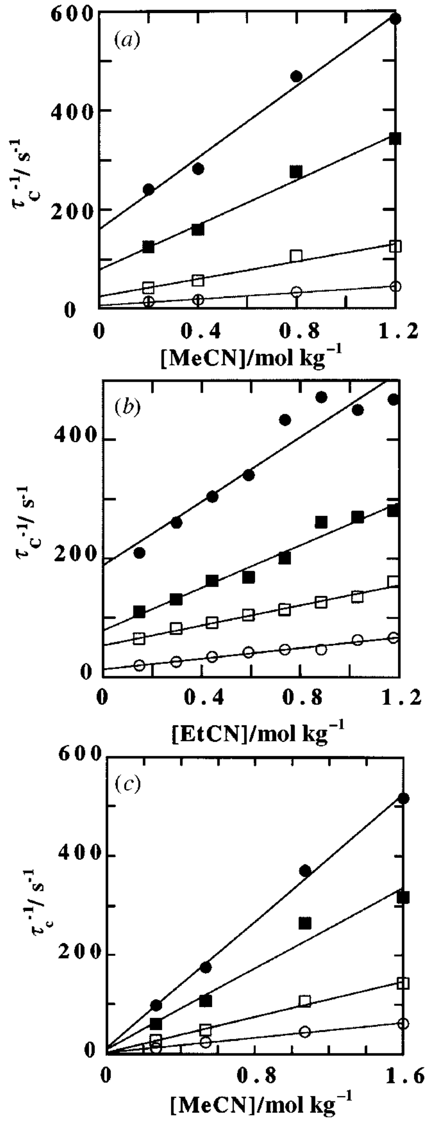
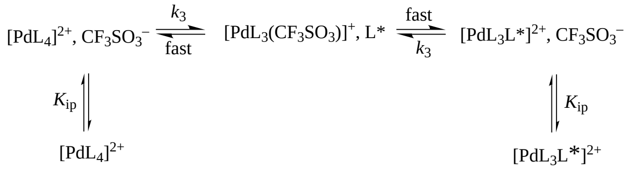


Fig. 2 Inverse of the mean lifetime of co-ordinated nitrile as a function of free nitrile concentration at different temperatures: (*a*) $[Pd(MeCN)_4]^{2+}$ **1**, ○ 297.4, □ 312.6, ■ 327.0, ● 337.0 K; (*b*) $[Pd(EtCN)_4]^{2+}$ **2**, ○ 301.5, □ 316.3, ■ 326.4, ● 336.4 K; (*c*) $[Pd(MeCN)_4]^{2+}$ **5**, ○ 300.1, □ 313.2, ■ 328.2, ● 338.2 K



Scheme 1

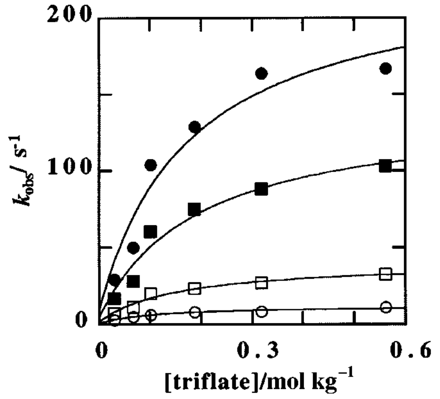


Fig. 3 Inverse of the mean lifetime of co-ordinated acetonitrile at $[Pd(MeCN)_4]^{2+}$ as a function of triflate concentration at different temperatures. No free acetonitrile was added. ○ 296.8, □ 311.3, ■ 326.3, ● 337.2 K

Also in the absence of added free nitrile the peak from co-ordinated nitrile is substantially broadened due to exchange. This is due to the presence of small amounts of free nitrile (not detectable by NMR spectroscopy) liberated from the complex in its interaction with the solvent and/or the counter ion. In one series of experiments, designed to study the counter-ion dependence, τ_C^{-1} for the palladium acetonitrile compounds **1** and **5** was determined from the peak width of co-ordinated MeCN, W_C, by use of equation (5) (Table S2, SUP 57305).

$$\tau_C^{-1} = \pi W_C - (1/T_2^*) \qquad (5)$$

These experiments were performed in the absence of added free acetonitrile (giving a k_2 term of 0) and at different counter-ion concentrations and temperatures. For the tetrafluoroborate compound **5** there was no observable counter-ion dependence and the mean of τ_C^{-1} measured equals k_1 determined by equation (4) within experimental errors. The data from this experiment were used to evaluate the activation parameters for the k_1 path. Rate constants and activation parameters obtained by a fit of the Eyring equation to the temperature dependencies of k_1 and k_2 are given in Table 1.

In the case of the triflate compound **1**, on the other hand, there is a strong triflate dependence and plots of τ_C^{-1} *versus* $[CF_3SO_3^-]$ show saturation kinetics according to equation (6)

$$\tau_C^{-1} = k_1 + \frac{k_3K_{ip}[CF_3SO_3^-]}{1 + K_{ip}[CF_3SO_3^-]} \qquad (6)$$

(*cf.* Fig. 3), where k_3 and K_{ip} are constants as defined in Scheme 1. The value of K_{ip} is ionic strength dependent. For low $[CF_3SO_3^-]$ equation (6) can be approximated to $\tau_C^{-1} = k_3K_{ip}$, and so the ionic strength was kept approximately constant at

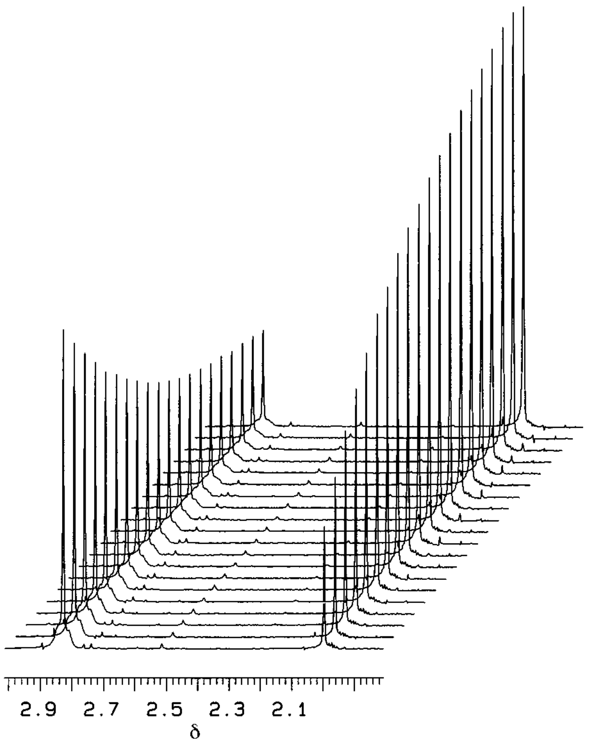


Fig. 4 Proton NMR spectra recorded every 3 min after mixing CD_3CN and $[Pt(MeCN)_4]^{2+}$ **3**. $c_M = 31.2$ mmol kg^{-1}, $[L] = 0.601$ mol kg^{-1} and $T = 324.6$ K. First spectrum 514 s after mixing and last after 3934 s. The accumulation time for each spectrum was 35 s.

0.17 mol kg^{-1}. At higher $[CF_3SO_3^-]$, where equation (6) can be approximated to $\tau_C^{-1} = k_3$ the ionic strength was allowed to vary. A fit of equation (6) to the data with k_1 (0.59 s^{-1} at 298 K) as a constant taken from the experiments with the tetrafluoroborate salt **5** gave the following values: $k_3^{300} = 12.5 \pm 1.3$ s^{-1} and $K_{ip}^{300} = 8 \pm 2$ kg mol^{-1}. In good agreement with this experimental value, a calculation of K_{ip} according to the Fuoss equation[18] with an average distance of 5 Å and an ionic strength of 0.17 mol kg^{-1} gives a value of 7 kg mol^{-1} for nitromethane solvent. Fitting the Eyring equation to the values of k_3 at different temperatures gives $\Delta H_3^{\ddagger} = 63 \pm 4$ kJ mol^{-1} and $\Delta S_3^{\ddagger} = -13 \pm 11$ J K^{-1} mol^{-1}.

Platinum complexes

For the slowly exchanging platinum complexes **3** and **4**, plots of peak areas of consecutive spectra (see Fig. 4) *versus* time in the isotopic labelling experiments yield two curves, corresponding to free and co-ordinated nitrile (Fig. 5). These curves were fitted by equation (7), where y denotes peak areas and C is the rate

$$y = y_\infty + (y_o - y_\infty)e^{-Ct} \qquad (7)$$

constant for isotopic exchange. The total rate of exchange, R_{ex}, was calculated from the average of the two values of C, by use of the McKay equation (8) (Table S3 SUP 57305).[19] Plots of

$$R_{ex} = \frac{C4c_M\,[L]}{(4c_M + [L])} \qquad (8)$$

$R_{ex}/4c_M$ *versus* [L] give straight lines with an intercept for both complexes (Fig. 6), validating the rate law (4). Rate constants and activation parameters obtained by a fit of the Eyring equation to the temperature dependencies of k_1 and k_2 are given in Table 1.

Mechanism

Nitrile exchange in nitromethane follows a two-term rate law (4). The k_2 term is interpreted as a direct attack by nitrile at the complex. The nitrile-independent k_1 path is well defined for all five complexes studied, although it is small for the tetrafluoroborate compound **5**. In this case the intercept is independent of the tetrafluoroborate concentration, and the most reasonable interpretation is a solvent path involving attack by nitromethane at the complex. A nitromethane solvent path was demonstrated in 1960 for chloride exchange at *trans*-$[PtCl_2(py)_2]$ (py = pyridine).[20] Exchange at $[Pd(MeCN)_4]^{2+}$ using a tetrafluoroborate salt of the complex in nitromethane has been reported earlier.[8] Our data for complex **5** agree fairly well with those given in ref. 8, from which an intercept of 4.0 s^{-1} at 322.6 K in the plots of k_{ex} *vs.* nitrile concentration can be derived. This should be compared to the value of 3.5 s^{-1} calculated from the present measurements. Also the value of the slope (k_2 as defined in the present paper), 194 ± 14 kg mol^{-1} s^{-1} at 322.6 K, calculated from the data in ref. 8 agrees relatively well with the values 165 ± 14 and 147 ± 13 kg mol^{-1} s^{-1} derived from the present experiments with compounds **1** and **5**.

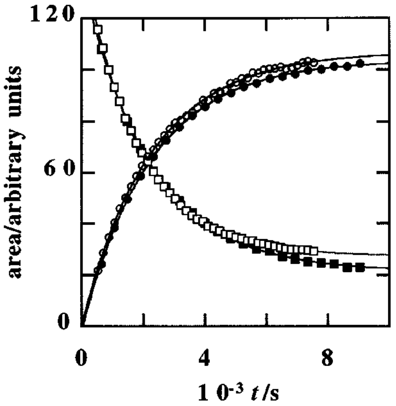


Fig. 5 Concentration decrease of co-ordinated, protonated and increase of free, protonated nitrile. ○, □ $[Pt(MeCN)_4]^{2+}$ **3**, conditions as in Fig. 4. ■, ● $[Pt(EtCN)_4]^{2+}$ **4**, $c_M = 20.5$ mmol kg^{-1}, $[L] = 0.589$ mol kg^{-1}, $T = 323.3$ K

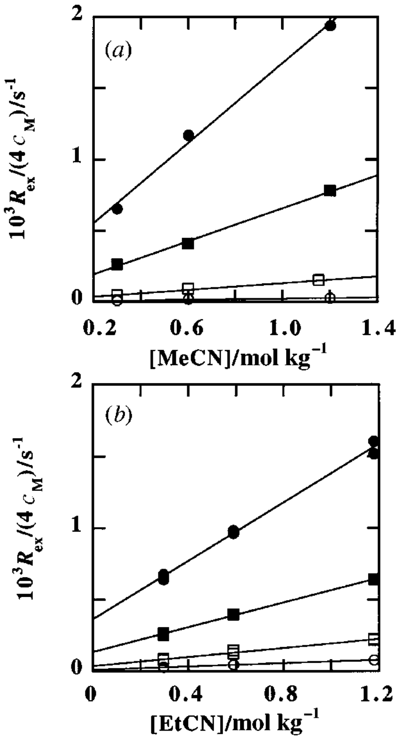


Fig. 6 Plots of $R_{ex}/4c_M$ as a function of free nitrile concentration at different temperatures: (*a*) $[Pt(MeCN)_4]^{2+}$ **3**, ○ 296.4, □ 309.0, ■ 324.6, ● 334.4 K; (*b*) $[Pt(EtCN)_4]^{2+}$ **4**, ○ 303.3, □ 313.1, ■ 323.2, ● 333.3 K

An interpretation of the k_1 path for the triflate compounds **1**–**4** simply as a rate-determining reaction with the solvent can be excluded due to the large difference observed between the triflate and tetrafluoroborate salts of $[Pd(MeCN)_4]^{2+}$ **1** and **5**. Funahashi and co-workers[11] have recently also observed a triflate-dependent k_1 path in a similar system. The saturation kinetics observed for **1** is compatible with an Eigen–Wilkins type mechanism involving formation of an ion pair in a fast pre-equilibrium followed by intramolecular reversible substitution of nitrile for triflate in the inner co-ordination sphere of the complex, according to Scheme 1. An ion-pair mechanism of this type could explain the large contribution of triflate, in spite of its relatively low nucleophilicity. Tetrafluoroborate should form ion pairs of comparable stability, but whereas triflate is known to be able to co-ordinate to platinum metals[21] tetrafluoroborate is non-co-ordinating and the formation of ion pairs is not expected to result in nitrile exchange. Thus, to summarize, we can identify three parallel exchange pathways for the triflate compound, **1**. Apart from the direct nitrile exchange described by k_2, there should be a small nitromethane solvent path identical to the k_1 path determined for the tetrafluoroborate compound **5**, and an additional triflate-dependent pathway (k_3) *via* intramolecular exchange in the ion pair formed between the complex and triflate.

In the case of $[Pt(EtCN)_4]^{2+}$ **4**, two experiments with different platinum and thus triflate concentrations were performed at each temperature and [EtCN], without giving significantly different $R_{ex}/4c_M$. In the case of platinum, therefore, low concentrations of triflate give an insignificant contribution to the k_1 pathway. The intercept would then be attributed to a solvent path, although a counter-ion interaction with the platinum complexes cannot be excluded. Thus, the values of k_1, $\Delta S_1^\ddagger$ and $\Delta H_1^\ddagger$ in Table 1 are composite quantities for complexes **1** and **2**, but probably not for **3** and **4**.

The rate constants for the direct nitrile exchange, k_2, derived from the present experiments are of the expected order of magnitude, intermediate between those for $[M(H_2O)_4]^{2+}$ and $[M(Me_2S)_4]^{2+}$ for both metals. The interaction between metal and nitrile is mainly of σ-donor character as concluded from the increase of ν(C–N) upon complexation. As usual for weakly interacting ligands, the reactivity ratio between Pd and Pt is about six orders of magnitude. The exchange of methyl for ethyl on the nitrile has little effect on the rates, since the linearity of the N–C–C axis gives rise to little steric retardation.[22] All activation entropies are negative, speaking in favour of associative activation.

To conclude, it is obvious from the present experiments and from the recent work by Yagyu *et al.*[11] that triflate can compete with weakly co-ordinating ligands through an ion-pairing mechanism. Noteworthy, we have earlier observed a significant intercept in the exchange data for oxygen-bonded Me_2SO at platinum(II) in nitromethane that might have a similar origin.[5] In addition, a small but still significant contribution from a nitromethane solvent path cannot be excluded, in particular when exchange of weakly co-ordinating ligands is studied.

Acknowledgements

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