Mono- and Dinuclear Carbonyl Complexes of (1,4,7-Trimethyl-1,4,7-triazacyclononane)rhodium(I): Facile Migration of a C(O)OMe Ligand at a Dinuclear Rh(μ-CO)$_2$Rh Core

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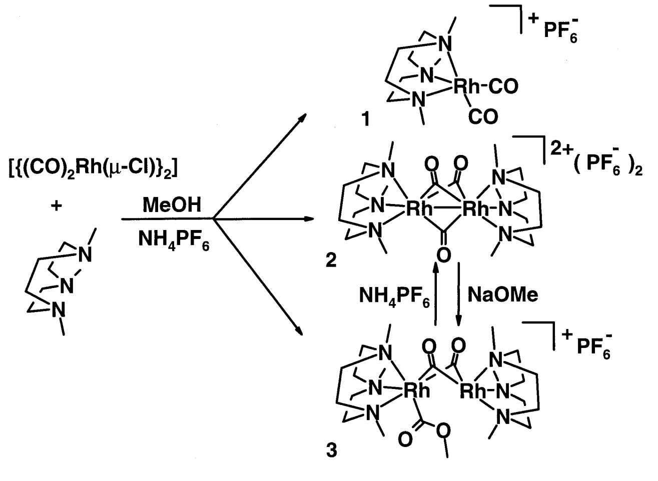
The reaction of 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn*) with [{(CO)$_2$Rh(μ-Cl)}$_2$] in methanol at 0°C, followed by the addition of NH$_4$PF$_6$, results in the formation of the mononuclear carbonyl complex [Cn*Rh(μ-CO)$_2$]PF$_6$ ([**1**]PF$_6$), the dinuclear carbonyl complex [Cn*Rh(μ-CO)$_3$RhCn*](PF$_6$)$_2$ {[**2**](PF$_6$)$_2$} and the dinuclear methoxycarbonyl complex [Cn* Rh(C(O)OMe)(μ-CO)$_2$RhCn*]PF$_6$ ([**3**]PF$_6$). The reaction of [**2**](PF$_6$)$_2$ with NaOMe results in formation of [**3**]PF$_6$ by the attack of the methoxide at a bridging carbonyl. Treatment of [**3**]PF$_6$ with NH$_4$PF$_6$ regenerates [**2**](PF$_6$)$_2$, thus showing that the methoxylation of [**2**](PF$_6$)$_2$ is reversible. The structures of [**1**]PF$_6$, [**2**](PF$_6$)$_2$ and [**3**]PF$_6$ have been determined by single-crystal X-ray diffraction. For [**3**]PF$_6$ an unprecendented facile, reversible, migration of the C(O)OMe ligand between the two rhodium centres of the Rh(μ-CO)$_2$Rh core is observed.

Tridentate N-donor ligands ('N$_3$' ligands) have so far found a limited application in the area of the organometallic chemistry of rhodium. Interesting reactivities have however been reported for rhodium complexes with *fac*-coordinating 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn*) and [hydrotris(3,5-pyrazolyl)borate] (Tp^{Me2}) [1][2], and *mer*-coordinating pyridine-2,6-diimine (2,6-(C(R)=N-R')$_2$-C$_5$H$_3$N).[3] For ['N$_3$' Rh^I(cod)]$^+$, ['N$_3$' is Cn* or *N*-butyl-*N,N*-di-(2-pyridylmethyl)amine], we have recently reported on the oxidation of the cod ligand by H$_2$O$_2$ to a bicyclooxanonadiyl fragment.[4] In an extension of our explorative studies on the structure and reactivities of 'N$_3$' Rh sites, we now report on the carbonyl chemistry of Cn*Rh^I sites.

Results and Discussion

The reaction of the rigid *fac*-ligand Cn* with {[(CO)$_2$Rh(μ-Cl)]$_2$} in methanol at 0°C, followed by addition of NH$_4$PF$_6$, leads to the precipitation of a mixture of yellow [**2**](PF$_6$)$_2$ and orange [**3**]PF$_6$. Upon cooling of the filtrate, further precipitation of [**2**](PF$_6$)$_2$ and [**3**]PF$_6$ occurred, and a few bright-orange crystals of [**1**]PF$_6$ deposited (Scheme 1).

Scheme 1. Synthesis of [**1**]PF$_6$, [**2**](PF$_6$)$_2$ and [**3**]PF$_6$



From the solid mixture that was obtained by filtration, the crystals of [**1**]PF$_6$ were removed by hand. We were able to interconvert [**2**](PF$_6$)$_2$ and [**3**]PF$_6$ in the resulting mixture; reaction with approx. 5.5 mol NaOMe per mol of [**2**](PF$_6$)$_2$ in MeOH resulted in the quantitative formation of [**3**]PF$_6$. Treatment of the same mixture with approx. 7 mol NH$_4$PF$_6$ per mol of [**3**]PF$_6$ in MeOH under reflux resulted in quantitative conversion to [**2**](PF$_6$)$_2$ (Scheme 1). [**2**](PF$_6$)$_2$ and [**3**]PF$_6$ were isolated as pure compounds via these procedures. Attempts to prepare [**2**](PF$_6$)$_2$ by refluxing an acetone solution of [**1**]PF$_6$ resulted in the almost quantitative recovery of [**1**]PF$_6$. Attempts to prepare [**1**]PF$_6$ by exposure of an acetone solution of [**2**](PF$_6$)$_2$ to 40 bar CO were also unsuccessful.

Structure of [**1**]PF$_6$

The structure of [**1**]PF$_6$ was determined by single-crystal X-ray diffraction (Figure 1). Selected bond lengths and angles are given in Tables 1 and 2.

The cation [**1**]$^+$ contains two terminal carbonyl groups. The coordination geometry can best be described as a pseudo trigonal bipyramid. The equatorial positions are occupied by one carbonyl and two nitrogens of the Cn* ligand; the axial-positions by the second carbonyl and the

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Figure 1. Crystal structure of cation [**1**]$^+$

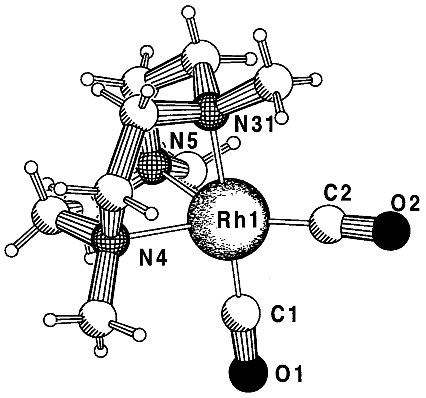


Table 1. Selected bond lengths [Å] for compounds [**1**]PF$_6$, [**2**](PF$_6$)$_2$ and [**3**]PF$_6$[a]

	[**1**]$^+$	[**2A**]$^{+[b]}$	[**2B**]$^{+[b]}$	[**3**]$^+$
N31−Rh1	2.139(3)	2.220(8)	2.213(9)	2.265(5)
N32−Rh2		2.197(10)	2.200(11)	2.257(6)
N4−Rh1	2.261(3)	2.189(7)	2.190(8)	2.278(6)
N5−Rh1	2.320(3)	2.189(7)	2.190(8)	2.256(5)
N6−Rh2		2.200(7)	2.194(7)	2.275(5)
N7−Rh2		2.200(7)	2.194(7)	2.262(5)
C1−Rh1	1.842(4)	2.049(9)	1.999(10)	2.114(8)
C1−Rh2		2.050(10)	1.993(11)	2.709(10)
C2−Rh1	1.827(4)	1.995(8)	2.010(8)	1.998(6)
C2−Rh2		2.014(8)	1.999(9)	1.910(6)
C3−Rh1		1.995(8)	2.010(8)	1.986(7)
C3−Rh2		2.014(8)	1.999(9)	1.907(7)
C1−O1	1.136(5)	1.121(12)	1.170(13)	1.216(9)
C2−O2	1.141(5)	1.166(10)	1.167(11)	1.189(8)
C3−O3		1.166(10)	1.167(11)	1.202(8)
C1−O4				1.355(9)
C4−O4				1.436(9)
Rh1−Rh2		2.5888(14)	2.5930(12)	2.6512(6)

[a] For atom labelling see Figures 1, 2, and 3. – [b] In accord with the labelling for [**3**]$^+$, the symmetry related atoms of N4, N6, C2 and O2 (obtained by applying m) in [**2A**]$^{2+}$ and [**2B**] $^{2+}$, are presented as N5, N7, C3 and O3, respectively, for reasons of comparison.

third nitrogen of Cn*. Remarkably, the N donors in the trigonal plane (N4 and N5) span the smallest N−Rh−N angle [76.41(11)°]. In order to be closer to the ideal 120° angle for a trigonal bipyramid, these N donors would be expected to span the largest N−Rh−N angle.

The axial Rh−N distance [Rh1−N31: 2.139(3) Å] is shorter than the equatorial Rh−N distances. [Rh1−N4: 2.261(3) Å, Rh1−N6: 2.320(3) Å]. The Rh−C and C−O distances of the equatorial and the axial carbonyl groups of cation [**1**]$^+$ are equal within the experimental error (averaged distances: Rh−C: 1.83 Å, C−O: 1.14 Å) and are comparable to those in known five-coordinate (L)$_3$Rh^I(CO)$_2$ complexes.[5][6] In contrast to [**1**]$^+$, these are all neutral complexes containing a monoanionic ligand, mostly a Cp-derivative. (Observed range in Rh−C distances: 1.824−1.867 Å, C−O distances: 1.109−1.154 Å.) Thus far, the hydrotrispyrazolylborate (Tp$^{R,R'}$) complex [(Tp^{CF3,Me})Rh^I(CO)$_2$] was the only "five-coordinate" 'N$_3$'Rh^I(CO)$_2$ complex with a reported X-ray structure.[6] In this complex, one of the three pyrazolyl groups is only weakly bound to the apical position in a square pyramidal geometry [Rh−N: 2.636(5)]. The basal Rh−N distances are 2.116(4) and 2.114(5) Å. Other reported bond lengths are: Rh−C: 1.824(7), 1.832(9) Å, C−O: 1.145(12), 1.146(9) Å. In solution [(Tp^{CF3,Me})Rh^I(CO)$_2$] behaves like other [Tp$^{R,R'}$Rh^I(CO)$_2$] derivatives in that it gives rise to equilibria between four and five coordination.[7]

Table 2. Selected bond angles [°] for compounds [**1**]PF$_6$, [**2**](PF$_6$)$_2$, and [**3**]PF$_6$[a]

	[**1**]$^+$	[**2A**]$^{+[b]}$	[**2B**]$^{+[b]}$	[**3**]$^+$
N31−Rh1−N4	81.87(10)	81.8(3)	81.1(3)	79.5(2)
N31−Rh1−N5	79.41(10)	81.8(3)	81.1(3)	79.2(2)
N4−Rh1−N5	76.41(11)	81.0(4)	80.8(4)	79.5(2)
N32−Rh2−N6		81.1(3)	81.3(3)	78.6(2)
N32−Rh2−N7		81.1(3)	81.3(3)	78.4(2)
N6−Rh2−N7		81.0(4)	81.2(4)	79.4(2)
N31−Rh1−C1	177.65(14)	179.6(4)	178.4(5)	172.5(3)
N32−Rh2−C1		179.2(4)	179.1(5)	
N31−Rh1−C2	95.91(14)	97.2(3)	97.6(4)	97.0(2)
N32−Rh2−C2		98.6(3)	97.7(3)	107.5(2)
N31−Rh1−C3		97.2(3)	97.6(4)	93.6(2)
N32−Rh2−C3		98.6(3)	97.7(3)	104.2(3)
N4−Rh1−C1	95.79(13)	98.5(3)	100.1(3)	96.6(3)
N4−Rh1−C2	144.29(18)	96.6(3)	97.3(4)	98.0(2)
N4−Rh1−C3		177.5(3)	177.8(3)	173.1(2)
N5−Rh1−C1	100.14(14)	98.5(3)	100.1(3)	93.8(3)
N5−Rh1−C2	138.52(17)	177.5(3)	177.8(3)	175.7(2)
N5−Rh1−C3		96.6(3)	97.3(4)	99.3(2)
N6−Rh2−C1		98.3(3)	99.4(3)	
N6−Rh2−C2		97.1(3)	96.8(3)	96.9(3)
N6−Rh2−C3		178.1(3)	177.9(3)	174.1(3)
N7−Rh2−C1		98.3(3)	99.4(3)	
N7−Rh2−C2		178.1(3)	177.9(3)	172.4(2)
N7−Rh2−C3		97.1(3)	96.8(3)	96.0(2)
O1−C1−Rh1	177.6(4)	140.8(8)	138.7(9)	126.6(6)
O1−C1−Rh2		140.9(8)	140.3(9)	
O2−C2−Rh1	176.8(4)	141.5(7)	139.1(8)	134.7(5)
O2−C2−Rh2		137.9(7)	140.2(8)	139.9(5)
O3−C3−Rh1		141.5(7)	139.1(8)	134.8(5)
O3−C3−Rh2		137.9(7)	140.2(8)	139.4(5)
Rh1−C1−Rh2		78.3(3)	81.0(4)	
Rh1−C2−Rh2		80.4(3)	80.6(3)	85.4(3)
Rh1−C3−Rh3		80.4(3)	80.6(3)	85.8(3)
C1−Rh1−C2	85.95(16)	82.5(3)	81.2(3)	89.9(3)
C1−Rh2−C2		82.0(3)	81.6(3)	
C1−Rh1−C3		82.5(3)	81.2(3)	90.3(3)
C1−Rh2−C3		82.0(3)	81.6(3)	
C2−Rh1−C3		85.8(5)	84.6(6)	82.7(3)
C2−Rh2−C3		84.8(5)	85.2(5)	87.2(3)
C1−Rh1−Rh2		50.8(3)	49.4(3)	68.2(3)
C2−Rh1−Rh2		50.1(2)	49.5(3)	45.9(2)
C3−Rh1−Rh2		50.1(2)	49.5(3)	45.8(2)
C1−Rh2−Rh1		50.8(2)	49.6(3)	
C2−Rh2−Rh1		49.5(2)	49.9(2)	48.7(2)
C3−Rh2−Rh1		49.5(2)	49.9(2)	48.4(2)
O1−C1−O4				120.3(7)
O4−C1−Rh1				112.6(5)
C1−O4−C4				115.2(6)

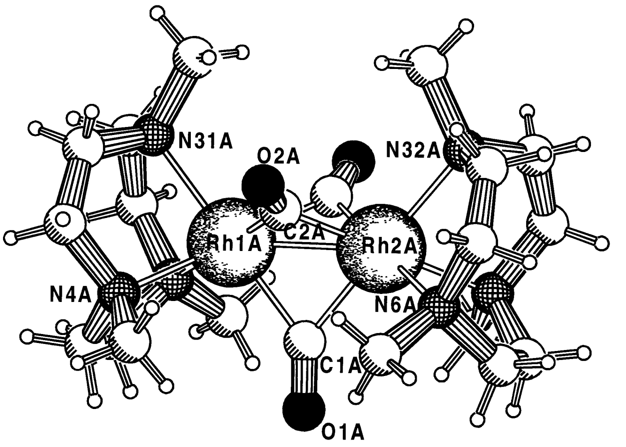
[a] For atom labelling see Figures 1, 2, and 3. – [b] In accord with the labelling for [**3**]$^+$, the symmetry related atoms of N4, N6, C2, and O2 (obtained by applying m) in [**2A**]$^{2+}$ and [**2B**] $^{2+}$, are presented as N5, N7, C3, and O3, respectively, for reasons of comparison.

The positions of the terminal ν_{CO} bands in the IR spectra of [**1**]PF$_6$ in the solid state (KBr: 2054 and 1962 cm^{-1}) differ significantly from those in solution (CH$_3$CN: 2063 and 1980 cm^{-1}). A square pyramidal or even a square planar geometry for [**1**]PF$_6$ in solution can therefore not be excluded. The latter geometry however seems unlikely, as it would require the rather rigid Cn* ligand to be κ^2-coordinated in solution. The ^{1}H-NMR spectrum of [**1**]PF$_6$ in [D$_6$]acetone or CD$_3$CN shows one singlet for the three N$-$CH$_3$ groups of the Cn* ligand, and one AA′BB′-multiplet pattern for its diastereotopic N$-$CH$_a$H$_b-$ protons. The ^{13}C-spectrum of [**1**]PF$_6$ shows only one doublet at δ = 189 ($^1J_{C-Rh}$ = 73 Hz) for both carbonyl groups. The equivalence of its N$-$CH$_2-$ and its N$-$CH$_3$ groups in the ^{1}H-NMR spectrum and the two carbonyls in the ^{13}C-spectrum must result from the rapid exchange of positions by Cn* nitrogens and carbonyl carbons at room temp.

Structure of [2](PF$_6$)$_2$

Bright yellow crystals of compound [**2**](PF$_6$)$_2$ were obtained from a saturated MeOH solution. From one of these crystals the structure of the cation [**2**]$^{2+}$ was determined by X-ray diffraction (Figure 2). Selected bond lengths and angles are given in Tables 1 and 2.

Figure 2. Crystal structure of cation [**2A**]$^{2+}$



In the crystal structure two independent cations, [**2A**]$^{2+}$ and [**2B**]$^{2+}$, are found per unit cell. Each cation only slightly deviates from C_{2v} symmetry. A crystallographic mirror-plane passes through Rh1, Rh2, and C1. The two rhodium centers are bridged via three carbonyl groups. The coordination geometry of the two (μ-CO)$_3$ bridged rhodium atoms can best be described as distorted octahedral. In contrast to [**1**]$^+$, all N$-$Rh$-$N angles in [**2A**]$^{2+}$ and [**2B**]$^{2+}$ are found at approx. 81°.

The rather short Rh$-$Rh distances of the two independent cations, Rh1A$-$Rh2A 2.5888(14) and Rh1B$-$Rh2B 2.5930(12) Å, are in accordance with a Rh$-$Rh single bond, resulting from application of the 18 VE rule. Theoretical calculations however indicated that actual M$-$M binding in M(d8)(μ-CO)$_3$M(d8) systems is much weaker.[8] The various Rh$-$N, Rh$-$C, and C$-$O distances are equal within experimental error (averaged distances: Rh$-$N: 2.20 Å, Rh$-$C: 2.01 Å, C$-$O: 1.16 Å). There are a few literature reports of complexes containing the [Rh(μ-CO)$_3$Rh]$^{2+}$ core.[9] The distances and angles of the [Rh(μ-CO)$_3$Rh]$^{2+}$ core of [**2**](PF$_6$)$_2$ compare well with those of [Rh(μ-CO)$_3$Rh]$^{2+}$ cores that have previously been characterized by single crystal X-ray diffraction; They involve 'N$_3$' ligands, viz. methyl(trispyrazolyl)gallate[10] and two macrocyclic hexaamine-type ligands,[11] and a tripod 'O$_3$' ligand.[12] On the basis of spectral and analytical data, complexes containing the [Rh(μ-CO)$_3$Rh]$^{2+}$ core have been proposed with the 'N$_3$' ligands tris(pyrazolyl-1-yl)methane,[13] a macrocyclic hexaamine[14] and hydrotris(pyrazolyl)borate.[15] For the 'S$_3$' ligand 2,5,8-trithia[9]-*o*-cyclophane it was reported that two ['S$_3$'Rh(CO)$_2$]$^+$ species exist in equilibrium with ['S$_3$'Rh(μ_2-CO)$_3$Rh'S$_3$']$^{2+}$ [16], in marked contrast with our own observations for ['N$_3$'Rh(CO)$_2$]$^+$ and ['N$_3$'Rh(μ_2-CO)$_3$Rh'N$_3$']$^{2+}$ (vide supra).

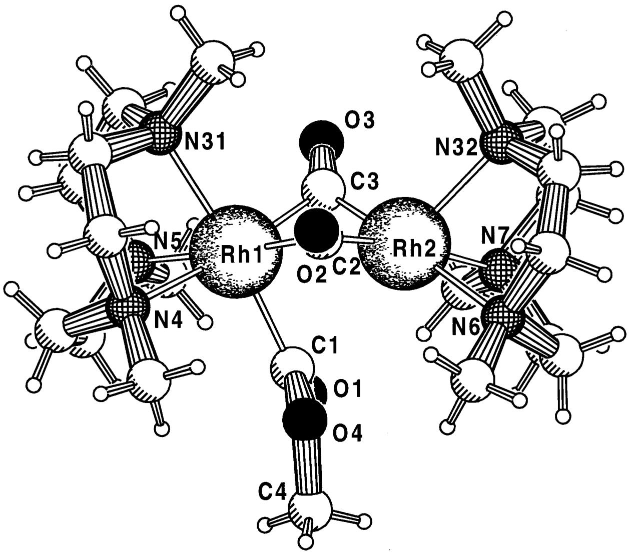
The IR band at 1810 cm^{-1} (CH$_3$CN) and the triplet ^{13}C-NMR signal at δ = 222 ($^1J_{C-Rh}$ = 28.7 Hz) indicate that the tri(μ-carbonyl) bridge is maintained in solution. The ^{1}H-NMR and ^{13}C-NMR signals for the two Cn* ligands show that [**2**]$^{2+}$ has an effective D_{3h} symmetry in solution. The N$-$CH$_2-$ groups are observed as one singlet in the ^{1}H-NMR spectrum in [D$_6$]acetone, but the chemically inequivalent *endo*- and *exo*-protons are observed as the expected AA′BB′ multiplet in CD$_3$CN.

[**2**](PF$_6$)$_2$ must be stored in the dark, since exposure to normal (glass-filtered) daylight results in a colour change from yellow, via intermediate green,[17] to dark blue, both in the solid state and in CH$_3$CN solution. The nature of the resulting blue compound is currently under investigation.[18]

Structure of [3]PF$_6$

Pale orange crystals of [**3**]PF$_6$ were obtained from a saturated MeOH solution, and the structure of cation [**3**]$^+$ was determined by X-ray diffraction (see Figure 3). Selected bond lengths and angles are given in Tables 1 and 2.

Figure 3. Crystal structure of cation [**3**]$^+$

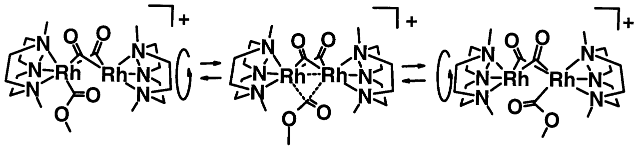


Comparison of Figures 2 and 3 shows that one of the three μ-carbonyl groups in [**2**]$^{2+}$ has been converted to a methoxycarbonyl group in [**3**]$^+$. This group is bound to only one of the two rhodium centres, at a Rh1−C1 distance of 2.114(8) Å, thus leaving the other rhodium centre apparently coordinatively unsaturated at a Rh2−C1 distance of 2.709(10) Å. The Rh1−C1 distance in [**3**]$^+$ is relatively long compared to those in previously reported Rh−C(O)OR complexes, viz. 1.918(9),[19] 2.041(5)[20] and 2.088(11)[21]Å. These complexes are all Rh^{III}-complexes. Ir−C distances in Ir−C(O)OR complexes have been found in the range 2.005 to 2.084 Å,[22] with the exception of a value of 2.20(4) Å reported for Ir−C(O)OMe in $[Ir_4(CO)_{11}\{C(O)OMe\}]^-$.[23] The Rh−Rh distance in [**3**]$^+$, 2.6512(6) Å, is somewhat elongated compared to that in [**2**]$^{2+}$, perhaps indicating the absence of a Rh−Rh bond in [**3**]$^+$. This would make Rh1 a 18 VE, six-coordinate Rh^I site and Rh2 a 16 VE, five-coordinate Rh^I site. Strikingly, the Cn* ligands in [**3**]$^+$ are found to be bound equally strongly to Rh1 and Rh2. Also there appear to be no significant differences between the Rh−N distances for N trans to μ-CO and N trans to the methoxycarbonyl-group or the vacant site. The average Rh−N distance in [**3**]$^+$, 2.26 Å, is approx. 0.06 Å longer than that in [**2**]$^+$. The largest difference between [**2**]$^+$ and [**3**]$^+$ is seen in the bonding of the bridging carbonyls. The addition of a methoxy anion to one of the three carbonyls in [**2**]$^+$ has resulted in an asymmetric coordination of the remaining two bridging carbonyls. They are bound approx. 0.1 Å more tightly, and their O−C−Rh angles are approx. 5° less acute for the "coordinatively unsaturated" Rh2. The Rh1−C2 and Rh1−C3 distances in [**3**]$^+$ are comparable to those found for [**2**]$^+$. In the IR spectrum of [**3**]PF_6 (KBr), three C−O stretching modes at 1771(w), 1708(s), and 1607(m) are observed. The first two are considered to be μ-CO vibrations, the latter is assigned to the carbonyl group of the C(O)OMe fragment. The appearance of a peak at *m/z* = 777 ([M − OMe]$^+$), besides peaks at *m/z* = 808 ([M]$^+$) and *m/z* = 663 ([M−PF_6]$^+$), in the FAB-MS spectrum shows loss of MeO^- under FAB conditions.

Fluxional Behaviour of in [**3**]$^+$ *in Solution: C(O)OMe Migration*

The IR spectrum of [**3**]PF_6 in CH_3CN [ν_{CO} 1774 (w), 1715 (s), 1618 (m)] is quite similar to that recorded in KBr, indicating that the structure of [**3**]$^+$ is maintained in solution. In the ^{1}H-NMR spectrum of [**3**]$^+$ the methoxy protons are observed as a singlet at δ = 3.5. In [D$_6$]acetone at room temperature only two singlets are observed for both Cn* groups, one singlet for all the N−CH_3 groups and one for all the N−CH_2− groups. In the ^{1}H-NOESY spectrum of [**3**]PF_6 NOE contacts are observed between the methoxy group and the methyl and methylene protons of the Cn* ligands. As observed for [**2**]$^{2+}$, in CD_3CN the N−CH_2− signal splits into an AA′BB′ pattern. Apparently [**3**]$^+$ has effective D_{3h} symmetry in which the two Cn* ligands, and the N−CH_2− and N−CH_3 groups within the Cn* ligands are equivalent on the NMR timescale. In the room temperature ^{13}C-spectrum in CD_3CN, the 18 different carbons in the two distinct Cn* ligands found in the X-ray structure give only two averaged ^{13}C signals, one at δ = 58.0 for the twelve N−CH_2− groups and one at δ = 51.5 for the six N−CH_3 groups. This must result from a fast equilibrium in solution. Two triplet signals are observed for the carbonyl groups, one at δ = 248.1 ($^1J_{Rh-C}$ = 37.5 Hz) for the μ-CO groups and one at δ = 179.9 ($^1J_{Rh-C}$ = 17.3 Hz) for the carbonyl of the C(O)OMe ligand, with relative intensity of 2:1. The apparently equal coupling of the C(O)OMe carbonyl signal with both rhodium centres must be the result of a rapid migration of the methoxycarbonyl ligand between Rh1 and Rh2. (Figure 4) As a result, each Rh-atom becomes alternately five and six coordinate. The observed apparent $^1J_{Rh-C}$ of 17.3 Hz is quite small compared to that in other Rh−C(O)OR compounds (31−55 Hz)[19][20][21]. It converts to an actual value of 34.6 Hz, comparable to the literature values, under the assumption that $^3J_{Rh-C}$ in the static structure of [**3**]$^+$ is close to zero.

Figure 4. Proposed mechanism of methoxycarbonyl migration in [**3**]PF_6



We propose that the observed averaging of NMR signals for the N−CH_2− and the N−CH_3 groups of the two Cn* ligands in [**3**]$^+$ results from a combination of two fast processes: reversible migration of the C(O)OMe ligand between both Rh centres, and exchange of nitrogen donor atom positions at the five-coordinate rhodium centre. The latter is also observed in five-coordinate [**1**]$^+$ (vide supra).

We thank *Unilever Research laboratory Vlaardingen* for a generous supply of 1,4,7-trimethyl-1,4,7-triazacyclononane.

Experimental Section

General Procedures: All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents (p.a.) were deoxygenated by bubbling through a stream of N_2, or by the freeze-pump-thaw method. $[\{(CO)_2Rh(\mu\text{-}Cl)\}_2]$ was prepared according to a literature procedure.[24] 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn*) was generously supplied by Unilever Research. All other chemicals are commercially available and were used without further purification. − FT-IR: Perkin Elmer 1720X. − NMR: Bruker DPX200 (200 MHz and 50 MHz for ^{1}H and ^{13}C, respectively), Bruker AC300 (300 MHz and 75 MHz for ^{1}H and ^{13}C, respectively). Solvent shift reference for ^{1}H NMR: [D$_6$]acetone δ_H = 2.05, CD_3CN δ_H = 1.98. For ^{13}C NMR: [D$_6$]acetone δ_C = 29.50, CD_3CN δ_C = 1.28. − FAB-MS: VG7070E.

Preparation of a Mixture of [**1**]PF_6, [**2**]$(PF_6)_2$ *and* [**3**]PF_6: In a typical experiment 200 mg of (1.16 mmol) Cn* was dissolved in 15 ml of MeOH and the resulting solution was cooled to 0°C. 234 mg (0.6 mmol) of $[\{(CO)_2Rh(\mu\text{-}Cl)\}_2]$ was subsequently added and the orange solution was stirred for approximately 1 h. Evolution of a slight amount of gas was noticed. The addition of 800 mg (4.91 mmol) of NH_4PF_6, dissolved in 5 ml of MeOH, to the reaction mixture caused the precipitation of a mixture of [**2**]$(PF_6)_2$ and [**3**]PF_6, which was collected by filtration. Combined yield 650 mg, ca. 60% based on $[\{(CO)_2Rh(\mu\text{-}Cl)\}_2]$. The filtrate was used to isolate a minor fraction of compound [**1**]PF_6.

[**1**]PF$_6$: [**1**]PF$_6$ was obtained as bright orange crystals, suitable for X-ray diffraction, by cooling the filtrate of the reaction mixture described above to −30°C. Besides further precipitation of [**2**](PF$_6$)$_2$ and [**3**]PF$_6$ a small amount of bright orange crystals of [**1**]PF$_6$ slowly deposited after some days. A few large crystals of [**1**]PF$_6$ could be isolated (hand-picking) from the resulting solid mixture.− ^{1}H NMR (200 MHz, CD$_3$CN): δ = 3.3−2.8 (m, 12 H, N−*CH$_2$*−), 3.19 (d, 9 H, $^3J_{\mathrm{Rh-H}}$ = 1 Hz, N−*CH$_3$*). − ^{13}C NMR (50 MHz, CD$_3$CN): δ = 189 (d, $^1J_{\mathrm{Rh-C}}$ = 73 Hz, Rh−*C*O), 59.6 (N−*CH$_2$*−), 55.3 (N−*CH$_3$*). − FT-IR (KBr): ṽ = 2054 cm^{-1}, 1962 (CO). − FT-IR (CH$_3$CN): ṽ = 2063 cm^{-1}, 1980 (CO). − FAB-MS; *m/z*: 273 [M−(CO)$_2$−PF$_6$−H]$^+$. − CHN analysis was not performed due to the small amount of pure [**1**]PF$_6$ obtained.

[**2**](PF$_6$)$_2$: 800 mg (4.91 mmol) of NH$_4$PF$_6$ was added to 600 mg of the solid mixture of [**2**](PF$_6$)$_2$ and [**3**]PF$_6$, prepared as decribed above. 15 ml of MeOH was subsequently added, and the mixture was refluxed (all solid material redissolved) for approximatly 10 min. After cooling to room temp., the MeOH solvent was partially evaporated. Compound [**2**](PF$_6$)$_2$ crystallized as bright yellow cubes from the solution at −30°C, and was collected by filtration. Yield 550 mg (ca. 80%). − ^{1}H NMR (200 MHz, CD$_3$CN): δ = 3.30−2.90 (m, 24 H , N−*CH$_2$*−), 2.84 (s, 18 H, N−*CH$_3$*). − ^{1}H NMR (200 MHz, [D$_6$]-acetone): δ = 3.44 (s, 24 H , N−*CH$_2$*−), 3.14 (s, 18 H, N−*CH$_3$*). − ^{13}C NMR (50 MHz, [D$_6$]-acetone): δ = 221.9 (t, $^1J_{\mathrm{Rh-C}}$ = 28.7 Hz, μ$_2$-CO), 58.5 (N−*CH$_2$*−), 52.0 (N−*CH$_3$*). − FT-IR (KBr): ṽ = 1803 cm^{-1} (μ-CO). − FT-IR (CH$_3$CN): ṽ = 1810 cm^{-1} (μ-CO). − FAB-MS; *m/z*: 777 [M−PF$_6$]$^+$, 748 [M−CO−PF$_6$]$^+$, 604 [M−CO−2PF$_6$]$^+$, 316 [M−2PF$_6$]$^{2+}$. − Calculated for $C_{21}H_{42}F_{12}N_6O_3P_2Rh_2$: C 27.35, H 4.59, N 9.11 Found: C 27.33, H 4.57, N 8.98.

[**3**]PF$_6$: 100 mg (1.9 mmol) of NaOMe was added to 300 mg of the solid mixture of [**2**](PF$_6$)$_2$ and [**3**]PF$_6$, prepared as decribed above. 15 ml of MeOH was subsequently added, and the mixture was refluxed (all solid material redissolved) for approximatly 10 min. After cooling to room temp., the MeOH solvent was partially evaporated. Compound [**3**]PF$_6$ crystallized as pale orange needles from the solution at −30°C, and was collected by filtration. Yield 200 mg (ca. 70%). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 3.54 (s, 3 H, O*CH$_3$*), 2.90 (s, 24 H, N−*CH$_2$*−), 2.81 (d, $^3J_{\mathrm{C-Rh}}$ = 0.8 Hz, 18 H, N−*CH$_3$*). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 57.7 (N−*CH$_2$*−), 51.1 (N−*CH$_3$*), 50.9 (O*CH$_3$*) (^{13}C-carbonyl signals undetected, due to low solubility). − ^{1}H NMR (300 MHz, CD$_3$CN): δ = 3.52 (s, 3 H, O*CH$_3$*), 2.90−2.55 (m, 24 H, N−*CH$_2$*−), 2.76 (d, $^3J_{\mathrm{H-Rh}}$ = 0.80 Hz, 18 H, N−*CH$_3$*). − ^{13}C NMR (75 MHz, CD$_3$CN): δ = 248.1 (t, $^1J_{\mathrm{C-Rh}}$ = 37.5 Hz, μ-CO), 179.9 (t, $^1J_{\mathrm{C-Rh}}$ = 17.3 Hz, *C*(O)OMe), 58.0 (N−*CH$_2$*−), 51.5 (N−*CH$_3$*), 51.4 (O*CH$_3$*). − FT-IR (KBr): ṽ = 1771 cm^{-1} (w), 1708 (s) (μ-CO), 1607 (m) (C=O), 1048 (C−O). − FT-IR (CH$_3$CN): ṽ = 1774 cm^{-1} (w), 1715 (s) (μ-CO), 1618 (m) (C=O), (C−O) obscured by solvent vibrations. − FAB-MS; *m/z*: 808 [M]$^+$, 777 [M−OMe]$^+$, 663 [M−PF$_6$]$^+$, 604 [M−PF$_6$−OMe−CO]$^+$, 576 [M−PF$_6$−OMe−2CO]$^+$. − Calculated for $C_{22}H_{45}F_6N_6O_4PRh_2$: C 32.69, H 5.61, N 10.40 Found: C 32.33, H 5.37, N 10.06.

X-ray Structure Determination of [**1**]PF$_6$, [**2**](PF$_6$)$_2$ *and* [**3**]PF$_6$: Crystals of [**1**]PF$_6$, [**2**](PF$_6$)$_2$ and [**3**]PF$_6$ suitable for X-ray diffraction studies were obtained by cooling a saturated solution of the corresponding compound in MeOH to −30°C. Single crystals were mounted in air on glass fibres. Intensity data were collected at room temp. For all three compounds an Enraf-Nonius CAD4 single-crystal diffractometer was used, graphite monochromatized Cu-*Kα* radiation, θ-2θ-scan mode. Unit cell dimensions were determined from the angular setting of 25 reflections. Intensity data were corrected for Lorentz and polarization effects. Semi-empirical absorption correction (*Ψ*-scan) was applied for all three compounds.[25]

Table 3. Crystallographic data for compounds [**1**]PF$_6$, [**2**](PF$_6$)$_2$, and [**3**]PF$_6$

	[**1**]PF$_6$	[**2**](PF$_6$)$_2$	[**3**]PF$_6$
Emperical formula	$C_{11}H_{21}F_6N_3O_2PRh$	$C_{21}H_{42}F_{12}N_6O_3P_2Rh_2$	$C_{22}H_{45}F_6N_6O_4PRh_2$
Crystal size [mm]	0.60 × 0.35 × 0.28	0.42 × 0.18 × 0.11	0.32 × 0.16 × 0.10
Formula weight	475.19	922.37	808.43
Temperature [K]	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P\ 2_1/n$	$C\ 2/m$	$P\ 2_1/n$
a [Å]	8.87948(17)	20.790(3)	8.5949(4)
b [Å]	15.2246(3)	15.814(3)	13.1036(5)
c [Å]	12.9031(3)	22.051(5)	27.7555(13)
α [°]	90	90	90
β [°]	91.960(4)	116.61(2)	91.124(4)
γ [°]	90	90	90
V [Å^3]	1743.30(6)	6482(2)	3125.3(2)
$\rho_{\mathrm{calcd.}}$ [gcm^{-3}]	1.811	1.890	1.718
Z	2	8	4
Wavelength [Å]	1.54184	1.54184	1.54184
$F(000)$	952	3696	1640
θ range [°]	4.49−69.88	40.158−46.695	40.113−46.904
Index ranges	$-10 \le h \le 10$	$-26 \le h \le 23$	$0 \le h \le 10$
	$-18 \le k \le 18$	$0 \le k \le 19$	$-15 \le k \le 0$
	$-15 \le l \le 15$	$0 \le l \le 27$	$-33 \le l \le 33$
Measured reflections	12510	7215	6340
Unique reflections	3303	7032	5926
Observed reflections [$I_o > 2\sigma(I_o)$]	3254	5747	5172
Refined parameters	302	439	377
Goodness-of-fit on F^2	1.104	1.086	1.032
R [$I_o > 2\sigma(I_o)$]	0.0332	0.0686	0.0599
$wR2$[all data]	0.0786	0.1922	0.1553
ρ_{fin} (max/min) [e Å^{-3}]	0.915/−0.623	1.845/−2.748	1.430/−2.186

Structures were solved by the program system DIRDIF[26] using the program PATTY[27] to locate the heavy atoms and were refined with standard methods (refinement against F^2 of all reflections with SHELXL97[28]) with anisotropic parameters for the nonhydrogen atoms. For [**1**]PF_6 the hydrogens were initially placed at calculated positions and were subsequently refined freely. For [**2**]$(PF_6)_2$ and [**3**]PF_6 all hydrogens were refined riding on the parent atoms. Details of the crystal parameters, data collections and structure refinements are given in Table 3. Crystallographic data (tables of structure determinations summaries, lists of anisotropic displacement parameters, lists of atom coordinates and full lists of bond lengths and angles, excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-100725. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk].

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