

Syntheses, Structures, and Spectroscopic Properties of *cis,cis*- and *trans,cis*-[Ru(I)(Me)(CO)₂(α -diimine)] Complexes

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The syntheses, structures, and spectroscopic properties are reported for *trans,cis* and *cis,cis* isomers of [Ru(I)(Me)(CO)₂(α -diimine)] [α -diimine = *N,N'*-diisopropyl-1,4-diazabutadiene (*iPr*-DAB), pyridine-2-carbaldehyde *N*-isopropylimine (*iPr*-PyCa), 4,4'-dimethyl-2,2'-bipyridine (*dmb*)] which differ in their photochemical behaviour. The structures of *trans,cis*- and *cis,cis*-[Ru(I)(Me)(CO)₂(*iPr*-DAB)] have been determined by a single-crystal X-ray diffraction study. The crystals of both isomers are monoclinic and belong to the same *P*2₁/*n* space group with *Z* = 4. Refinement converged to *R* = 0.043 for the *trans,cis* isomer and to *R* = 0.065 for the *cis,cis* isomer. Both complexes have a distorted octahedral geometry, in the *cis,cis* isomer the methyl ligand is located in an equatorial, the iodide in an axial position.

According to the ¹H- and ¹³C-NMR and resonance Raman spectra the imine groups of the *iPr*-DAB ligand are inequivalent in the *cis,cis* isomer. The absorption spectra vary with the α -diimine, not so much with the isomeric structure of the complex. Both isomers possess two visible absorption bands, which, according to the resonance Raman spectra, belong to charge transfer transitions from mixed metal-halide orbitals to the α -diimine. The resonance Raman spectra show that this charge transfer excitation is accompanied, for both isomers, with an angular distortion of the methyl ligand. These spectral data show that the difference in photochemical behaviour of the two isomers is not due to a change in the excited state character.

Introduction

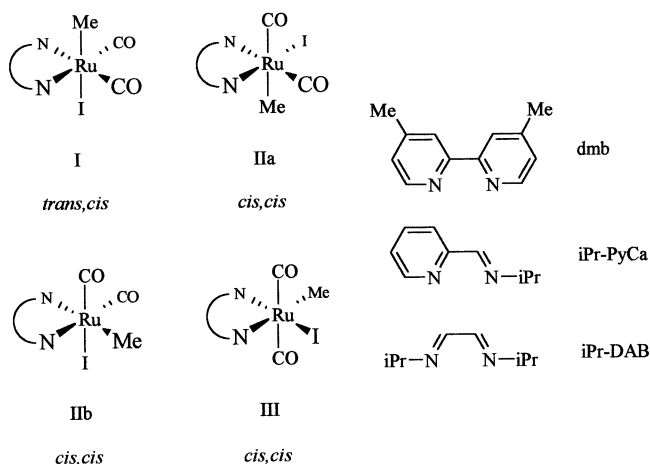
Many transition metal complexes having a lowest metal-to-ligand charge transfer (MLCT) excited state undergo efficient energy and electron transfer processes. Best studied in this respect are the complexes [Ru(bpy)₃]²⁺[1][2][3] and [Re(L')(CO)₃(bpy)]ⁿ⁺ (*n* = 0, 1; bpy = 2,2'-bipyridine; L' = halide, O- or N-donor ligand)[4][5][6][7][8], and their derivatives. The [Re(L')(CO)₃(α -diimine)]ⁿ⁺ complexes have the special property that variation of L' not only influences the energy and character of the lowest excited state but may also change its reactivity. For instance, the metal-metal-bonded complexes [(L_nM)Re(CO)₃(α -diimine)] [L_nM = (CO)₅Mn, (CO)₅Re, (CO)₄Co, Cp(CO)₂Fe] show a homolytic splitting of the Re-metal bond on irradiation with visible light.[4][9][10][11][12][13][14][14][15][16][17][18][19][20][21][22][23] Such homolysis reactions have also been observed for the Mn complexes [(CO)₅Mn-Mn(CO)₃(α -diimine)]^{[13][18]} and the Ru compounds [(L_nM)Ru(Me)(CO)₂(α -diimine)] [L_nM = (CO)₅Mn, (CO)₅Re, (CO)₄Co]^{[24][25]} and [Ru(SnPh₃)₂(CO)₂(α -diimine)].^{[25][26]} Similar photoreactions occur for the metal-alkyl (R) complexes [M(R)(CO)₃(α -diimine)] (M = Mn, Re)^{[27][28][29][30][31]}, [Ru(X)(R)(CO)₂(α -diimine)] (X = halide)^{[31][32]}, [Ir(R)(CO)(PAR₃)₂(mnt)]^[33], [Pt(Me)₄(α -diimine)]^[34], and [Zn(R)₂(α -diimine)]^[35], and even for the metal-halide complexes *mer*-[Mn(X)(CO)₃(α -diimine)].^{[36][37]} These homolysis reactions are assumed to

occur from a reactive ³ $\sigma\pi^*$ state in which σ represents the high-lying σ -bonding orbital, and π^* the lowest unoccupied orbital of the α -diimine ligand. Nearly all metal-metal-bonded complexes show at room temperature an efficient homolysis reaction, whereas the reactivity of the metal-alkyl complexes strongly depends on the nature of the alkyl group. For instance, the complexes [Re(R)(CO)₃(α -diimine)] (R = Et, Bzl) photodecompose into radicals with high quantum yield (Φ > 0.8), whereas the quantum yield is only 0.05 for the corresponding [Re(Me)(CO)₃(*iPr*-DAB)] complex.^[27] Similarly, in the case of [Ru(X)(R)(CO)₂(*iPr*-DAB)] (X = halide; R = Me, Et, *iPr*, Bzl), the isopropyl and benzyl complexes show a high efficiency for their homolysis reaction, whereas the methyl and ethyl complexes do not undergo such a reaction.^[32] A preliminary study showed that the complex *trans,cis*-[Ru(I)(Me)(CO)₂(*dmb*)] does not undergo a homolysis reaction, but is yet photolabile. It photoisomerises from its thermally stable *trans*(I,Me),*cis*(CO,CO) conformation into one of the two *cis,cis* isomeric forms. This photoproduct is photostable but thermally regenerates the parent *trans,cis* complex. In order to understand this remarkable behaviour, we have undertaken a structural and spectroscopic study of the *trans,cis* and *cis,cis* isomers. The results of this study are presented in this article.

The syntheses and molecular structures of several of these complexes have been first described by tom Dieck and

co-workers^{[38][39]}, while the complexes have been used for an acylation reaction by Vrieze and co-workers.^{[40][41]} The related complexes $[\text{Ru}(\text{Cl})_2(\text{CO})_2(\alpha\text{-diimine})]$ are known to form selectively stereoisomers.^[42] It will be shown that in the case of the complexes under study only one of the possible four stereoisomers presented in Figure 1 [structure **IIb**] is formed.

Figure 1. General molecular structures of the different isomers of $[\text{Ru}(\text{I})(\text{Me})(\text{CO})_2(\alpha\text{-diimine})]$ and of the α -diimine ligands used



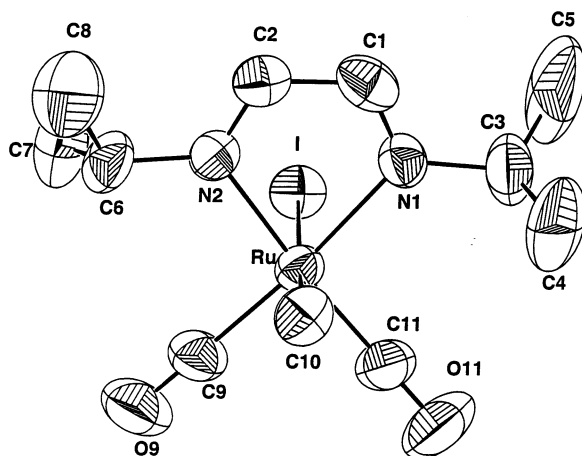
Results and Discussion

From the various *trans,cis*- and *cis,cis*- $[\text{Ru}(\text{I})(\text{Me})(\text{CO})_2(\alpha\text{-diimine})]$ complexes which were synthesised, two isomers are structurally characterised by X-ray diffraction, the others by spectroscopic means. After presentation of the X-ray data, attention will be paid to several aspects of the synthesis procedure, in particular to the identity of the intermediates **1** and **2** of this reaction. Finally, the spectroscopic data of the complexes will be reported and discussed.

Crystal Structure of *trans,cis*- $[\text{Ru}(\text{I})(\text{Me})(\text{CO})_2(i\text{Pr-DAB})]$

Table 1 presents the bond lengths and bond angles of the non-hydrogen atoms of the complex. The ORTEP drawing of Figure 2 shows its *trans,cis* geometry.

Figure 2. Molecular structure and selected atom numbering of the non-hydrogen atoms (ORTEP drawing at 50% probability) of *trans,cis*- $[\text{Ru}(\text{I})(\text{Me})(\text{CO})_2(i\text{Pr-DAB})]$



The *iPr*-DAB ligand is $\sigma(\text{N}1)-\sigma(\text{N}2)$ -bonded to the ruthenium centre, just as in the case of $[\text{Ru}(\text{Me})(\text{CO})_2(i\text{Pr-DAB})]^+\text{OTf}^-$ ^[43], $[\text{Ru}(\text{I})\{\text{C}(\text{O})\text{Me}\}(\text{CO})_2(i\text{Pr-DAB})]$ ^[43] and $[\text{Ru}(\text{I})(\text{Me})(i\text{Pr-DAB})(\text{nbdl})]$.^[44] The bite angle of $76.8(2)^\circ$, which causes the deviation from a regular octahedral structure, has also been found for these complexes. The Ru–Me bond length [2.183(9) Å] is comparable with those of the Ru–C bonds in the complexes $[\text{Ru}(\text{Me})(\text{CO})_2(i\text{Pr-DAB})]^+\text{OTf}^-$ [2.122(9) Å]^[43], $[\text{Ru}(\text{Me})(\text{Mn}(\text{CO})_5)(\text{CO})_2(i\text{Pr-PyCa})]$ [2.148(5) Å]^[45], $[\text{Ru}(\text{Me})(\text{CO})_2(i\text{Pr-DAB})]_2$ [2.152(5) Å]^[39] and $[\text{Ru}(\text{I})(\text{Me})(i\text{Pr-DAB})(\text{nbdl})]$ [2.222(13) Å].^[44] The Ru–I bond length [2.7998(9) Å] is comparable with that of the same bond in $[\text{Ru}(\text{I})(\text{Si}(\text{Me})_2\text{Ph})(\text{CO})_2(\text{NH}_2\text{CH}_2\text{C}_6\text{H}_5)_2]$ [2.848(1) Å]^[46], $[\text{Ru}(\text{I})\{\text{C}(\text{O})\text{Me}\}(\text{CO})_2(i\text{Pr-DAB})]$ [2.811(9) Å]^[43] and $[\text{Ru}(\text{I})(\text{Me})(i\text{Pr-DAB})(\text{nbdl})]$ [2.878(1) Å].^[44] It is somewhat larger than found for this bond in $[\text{Ru}(\text{I})_2(\text{CO})_2(i\text{Pr-DAB})]$ [2.711(8) Å]^[32] and $[\text{Ru}(\text{I})_2(\text{CO})_2(\text{pTol-DAB})]$ [2.708(1) Å]^[47] due to the much larger *trans* influence of the methyl group compared to I^- . The Ru–CO bonds (ca. 1.870 Å) are slightly longer than those of $[\text{Ru}(\text{Me})(\text{CO})_2(i\text{Pr-DAB})]^+\text{OTf}^-$ [1.847(9) Å]^[43], but comparable in length with those of $[\text{Ru}(\text{I})\{\text{C}(\text{O})\text{Me}\}(\text{CO})_2(i\text{Pr-DAB})]$ [1.874(7) Å].^[43]

Crystal Structure of *cis,cis*- $[\text{Ru}(\text{I})(\text{Me})(\text{CO})_2(i\text{Pr-DAB})]$

The bond lengths and angles are collected in Table 2, while the ORTEP drawing of the complex is presented in Figure 3.

Figure 3 confirms the *cis,cis* conformation of the complex with the methyl ligand in the equatorial plane and the iodide in an axial position. The structural data agree well with those of the *trans,cis* isomer discussed above and with those of the related complexes $[\text{Ru}(\text{I})\{\text{C}(\text{O})\text{Me}\}(\text{CO})_2(i\text{Pr-DAB})]$ ^[43], $[\text{Ru}(\text{Me})(\text{CO})_2(i\text{Pr-DAB})]^+\text{OTf}^-$ ^[43], $[\text{Ru}(\text{I})_2(\text{CO})_2(\text{pTol-DAB})]$ ^[47], $[\text{Ru}(\text{I})_2(\text{CO})_2(i\text{Pr-DAB})]$ ^[32], and $[\text{Ru}(\text{I})(\text{Me})(i\text{Pr-DAB})(\text{nbdl})]$.^[44] The complex has a distorted octahedral geometry [$\text{I}-\text{Ru}-\text{C}(10)$ $176.8(7)^\circ$]. The *iPr*-DAB ligand has a bite angle of $75.7(5)^\circ$, which is slightly smaller than found for the corresponding *trans,cis* complex [$76.8(2)^\circ$]. Since the CO ligand has a smaller *trans* influence than the methyl group, the Ru–I bond is shorter [2.754(2) Å] than in the case of *trans,cis*- $[\text{Ru}(\text{I})(\text{Me})(\text{CO})_2(i\text{Pr-DAB})]$ [2.7998(9) Å]. The bond lengths given in Table 2 for Ru–C(9) and Ru–C(11) are not very accurate. In the complex O(9) is divided in such a way that the CO and Me ligand are both equally distributed over the two possible positions, resulting in the introduction of two half O positions [O(9) and O(11)].

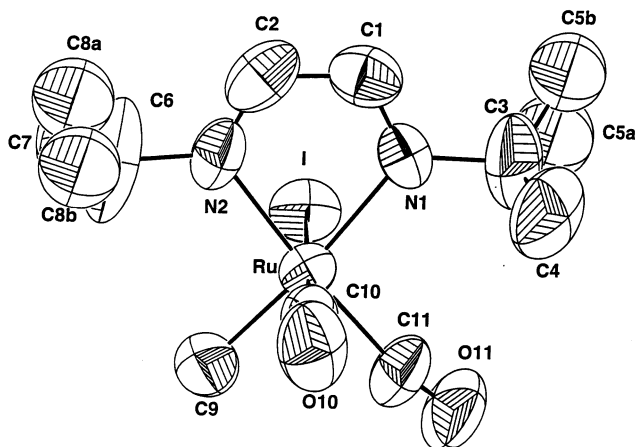
Mechanism of the Complex Formation

The reactions leading to the formation of the two isomers are presented in Scheme 1. The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with MeI in acetonitrile (MeCN) results in the formation of an unknown product **1a**, which has $\nu(\text{CO})$ vibrations at 2058(s), 1996(s), and 1637 cm^{-1} , and which is converted thermally into a second species **2a** having $\nu(\text{CO})$ bands at 2041(s) and $1974(\text{s})\text{ cm}^{-1}$. Both **1a** and **2a** react with an α -

Table 1. Bond lengths and angles of the non-hydrogen atoms of *trans,cis*-[Ru(I)(Me)(CO)₂(*i*Pr-DAB)] with standard deviations in parentheses

bond	length [Å]	bond	length [Å]	bond	length [Å]
Ru–I	2.7998(9)	C(1)–C(2)	1.48(1)	C(6)–C(7)	1.50(2)
Ru–C(9)	1.870(8)	C(1)–N(1)	1.25(1)	C(6)–C(8)	1.52(2)
Ru–C(10)	2.183(9)	C(2)–N(2)	1.26(1)	C(6)–N(2)	1.49(1)
Ru–C(11)	1.869(9)	C(3)–C(4)	1.52(2)	C(9)–O(9)	1.12(1)
Ru–N(1)	2.111(6)	C(3)–C(5)	1.37(2)	C(11)–O(11)	1.14(1)
Ru–N(2)	2.105(6)	C(3)–N(1)	1.51(1)		
bonds	angle [°]	bonds	angle [°]	bonds	angle [°]
I–Ru–C(9)	93.9(3)	C(10)–Ru–N(2)	85.1(3)	C(7)–C(6)–N(2)	109.2(8)
I–Ru–C(10)	175.4(2)	C(11)–Ru–N(1)	97.7(3)	C(8)–C(6)–N(2)	113.6(9)
I–Ru–C(11)	92.4(3)	C(11)–Ru–N(2)	172.8(3)	Ru–C(9)–O(9)	178.3(8)
I–Ru–N(1)	86.6(2)	N(1)–Ru–N(2)	76.8(2)	Ru–C(11)–O(11)	176.1(8)
C(9)–Ru–C(10)	89.9(4)	C(2)–C(1)–N(1)	117.2(7)	Ru–N(1)–C(1)	114.5(5)
C(9)–Ru–C(11)	88.5(4)	C(1)–C(2)–N(2)	116.6(8)	Ru–N(1)–C(3)	123.4(6)
C(9)–Ru–N(1)	173.8(3)	C(4)–C(3)–C(5)	120(1)	C(1)–N(1)–C(3)	122.0(7)
C(9)–Ru–N(2)	97.1(3)	C(4)–C(3)–N(1)	109.7(9)	Ru–N(2)–C(2)	114.9(5)
C(10)–Ru–C(11)	90.4(4)	C(5)–C(3)–N(1)	116(1)	Ru–N(2)–C(6)	123.9(5)
C(10)–Ru–N(1)	89.4(3)	C(7)–C(6)–C(8)	111.9(9)	C(2)–N(2)–C(6)	121.2(7)

Figure 3. Molecular structure and selected atom numbering of the non-hydrogen atoms (ORTEP drawing at 50% probability) of *cis,cis*-[Ru(I)(Me)(CO)₂(*i*Pr-DAB)]



diimine ligand. Thus, adding one equivalent of the α-diimine to a solution of **2a** results in the formation of *cis,cis*-[Ru(I)(Me)(CO)₂(α-diimine)], which has been structurally characterised with X-ray diffraction for α-diimine = *i*Pr-DAB (vide supra). The *cis,cis* isomers transform thermally within 3–7 days into the *trans,cis* isomers. On reaction of a *cis,cis* isomer with AgOTf, the halide (I[−]) is replaced by OTf[−]. This OTf complex can easily be converted into the *trans,cis* isomer by adding an excess of (*n*Bu)₄NI.

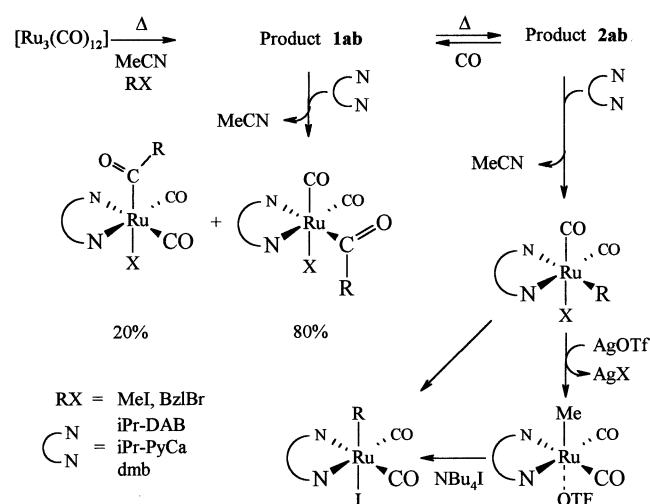
In order to elucidate the structure of the first product in the reaction sequence, **1a**, the reaction between [Ru₃(CO)₁₂] and MeI was first brought to completion with formation of product **2a**. This solution was then put under 1 atm of CO and after 2 h **2a** was completely converted into **1a**. On addition of one equivalent of *i*Pr-DAB, **1a** produced a mixture of two complexes in a 4:1 ratio, which are assigned to *cis,cis*- and *trans,cis*-[Ru(I){C(O)Me}{(CO)₂(*i*Pr-DAB)}], respectively, with the use of their ¹H-NMR spectra.^[48] Attempts to separate the two isomers failed. From the formation of

these products by reaction of **1a** with *i*Pr-DAB it is tentatively concluded that **1a** is the acyl derivative of **2a**.

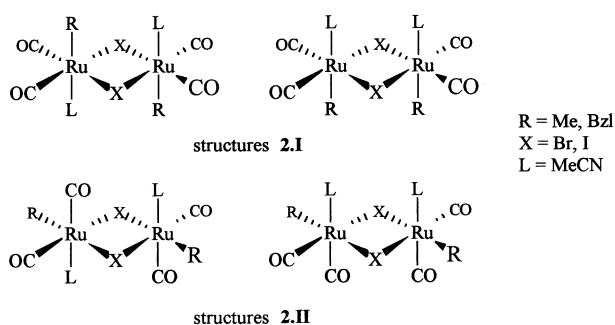
The structure of intermediate **2a** could not be determined by ¹H-NMR spectroscopy because of its low solubility and dynamic behaviour on the NMR time scale. Because of this, [Ru₃(CO)₁₂] was allowed to react with benzyl bromide (BzI) instead of with MeI. Intermediate **2b** is then formed as a major product with ν(CO) bands at 2042(s) and 1979(s) cm^{−1}, very similar to those of product **2a**. On addition of one equivalent of *i*Pr-DAB to **2b**, *cis,cis*-[Ru(Br)(BzI)(CO)₂(*i*Pr-DAB)] is formed, which in turn transforms within 30 min into the thermodynamically more stable *trans,cis* isomer. As **2a** and **2b** selectively produce the *cis,cis* isomers, these intermediates will neither represent *trans,cis,cis*-[Ru(X)(R)(CO)₂(MeCN)₂], analogous to *trans,cis,cis*-[Ru(Cl)₂(CO)₂(C₆H₅CN)₂]^[49] and *trans,cis,cis*-[Ru(Cl)₂(CO)₂(pyridine)₂]^[50], nor the thermodynamically unfavourable all-*cis*-[Ru(I)(Me)(CO)₂(MeCN)₂]. The ¹H-NMR spectrum of **2b** shows that the complex possesses one equivalent of both the BzI and acetonitrile (MeCN) ligands. Intermediates **2** are therefore proposed to be the dimeric species [Ru(X)(R)(CO)₂(MeCN)]₂ [X = I, R = Me (**2a**); X = Br, R = BzI (**2b**)]. Figure 4 presents four possible structures of this dimer. The ¹H-NMR spectrum of **2b** clearly shows a diastereotopic effect on the CH₂ group of the benzyl ligand. Since a similar effect is observed for *cis,cis*-[Ru(Br)(BzI)(CO)₂(*i*Pr-DAB)] it is concluded that structures **2.II** of Figure 4 are the most likely ones of **2**. For, if **2** had one of the **2.I** structures, a single resonance would have been observed for the CH₂ group, just as in the case of *trans,cis*-[Ru(Br)(BzI)(CO)₂(*i*Pr-DAB)]. The formation of the *cis,cis*-[Ru(X)(R)(CO)₂(α-diimine)] complexes from the dimeric intermediates [Ru(X)(R)(CO)₂(MeCN)]₂ (**2**) is then straightforward. The α-diimine substitutes MeCN (L) and chelation of this ligand occurs after rupture of an Ru–X bond. As the weaker Ru–X bond *trans* to R will preferably be broken, this chelation reaction leads to the formation of

Table 2. Bond lengths and angles of the non-hydrogen atoms of *cis,cis*-[Ru(I)(Me)(CO)₂(*i*Pr-DAB)] with standard deviations in parentheses

bond	length [Å]	bond	length [Å]	bond	length [Å]
Ru–I	2.754(2)	C(1)–N(1)	1.28(3)	C(6)–N(2)	1.51(2)
Ru–C(9)	1.97(2)	C(2)–N(2)	1.27(3)	C(6)–C(8a)	1.46(8)
Ru–C(10)	1.88(2)	C(3)–C(4)	1.50(4)	C(6)–C(8b)	1.40(5)
Ru–C(11)	2.01(2)	C(3)–N(1)	1.55(2)	C(9)–O(9)	0.99(3)
Ru–N(1)	2.15(1)	C(3)–C(5a)	1.29(8)	C(10)–O(10)	1.03(3)
Ru–N(2)	2.15(1)	C(3)–C(5b)	1.48(4)	C(11)–O(11)	0.97(3)
C(1)–C(2)	1.45(3)	C(6)–C(7)	1.50(4)		
bonds	angle [°]	bonds	angle [°]	bonds	angle [°]
I–Ru–C(9)	89.8(6)	C(11)–Ru–N(2)	174.5(7)	N(2)–C(6)–C(8a)	116(3)
I–Ru–C(10)	176.8(7)	N(1)–Ru–N(2)	75.7(5)	N(2)–C(6)–C(8b)	117(2)
I–Ru–C(11)	89.3(6)	C(2)–C(1)–N(1)	118(2)	C(8a)–C(6)–C(8b)	41(4)
I–Ru–N(1)	86.6(3)	C(1)–C(2)–N(2)	118(2)	Ru–C(9)–O(9)	175(2)
I–Ru–N(2)	88.3(4)	C(4)–C(3)–N(1)	105(1)	Ru–C(10)–O(10)	178(2)
C(9)–Ru–C(10)	88.1(8)	C(4)–C(3)–C(5a)	135(4)	Ru–C(11)–O(11)	169(2)
C(9)–Ru–C(11)	86.7(8)	C(4)–C(3)–C(5b)	113(2)	Ru–N(1)–C(1)	114(1)
C(9)–Ru–N(1)	173.0(7)	N(1)–C(3)–C(5a)	120(4)	Ru–N(1)–C(3)	124(1)
C(9)–Ru–N(2)	98.2(7)	N(1)–C(3)–C(5b)	118(2)	C(1)–N(1)–C(3)	121(1)
C(10)–Ru–C(11)	88.2(9)	C(5a)–C(3)–C(5b)	54(4)	Ru–N(2)–C(2)	115(1)
C(10)–Ru–N(1)	95.7(7)	C(7)–C(6)–N(2)	107(2)	Ru–N(2)–C(6)	125(1)
C(10)–Ru–N(2)	94.4(7)	C(7)–C(6)–C(8a)	115(3)	C(2)–N(2)–C(6)	119(2)
C(11)–Ru–N(1)	99.3(6)	C(7)–C(6)–C(8b)	136(2)		

Scheme 1. Proposed mechanism for the reaction of [Ru₃(CO)₁₂] with RX and α-diimine

a *cis,cis* isomer in which R occupies an equatorial position and the remaining halide an axial one.

Figure 4. Relevant structures of [Ru(X)(R)(CO)₂(MeCN)]₂

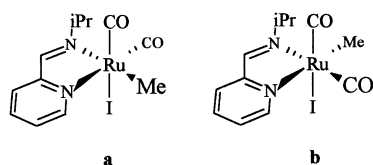
¹H- and ¹³C-NMR Spectra

The structures of the *cis,cis* and *trans,cis* isomers of the *i*Pr-PyCa and dmb complexes were not determined by X-ray diffraction but were instead deduced from their ¹H- and ¹³C-NMR spectra. The *trans,cis*-[Ru(I)(Me)(CO)₂(*i*Pr-DAB)] complex has C_s symmetry, and in agreement with this a simple pattern for the ¹H and ¹³C resonances is observed.^[40] The corresponding *cis,cis* complex has no symmetry anymore and two sets of proton and carbon signals are therefore expected for the coordinated *i*Pr-DAB ligand. These sets are indeed observed (see Experimental Section). However, due to the small difference in resonance frequencies in both the ¹H- and ¹³C-NMR spectra, the sets of signals can not be assigned separately to the two imine parts of the *i*Pr-DAB ligand positioned *trans* to the methyl and CO ligand, respectively.

For the complex *trans,cis*-[Ru(I)(Me)(CO)₂(dmb)] only one set of signals is observed in the NMR spectra, just as for *trans,cis*-[Ru(I)(Me)(CO)₂(bpy)].^[51] The *cis,cis* isomer shows again two sets of resonances in the ¹H- and ¹³C-NMR spectra, with small shifts comparable to those observed for the *i*Pr-DAB complex. These ¹H-NMR data exclude the formation of the *cis*(I,Me),*cis*(CO,CO) complex, with the iodide equatorial and the methyl group axial. The ¹H-NMR spectrum of *cis,cis*-[Ru(Cl)₂(CO)₂(R-PyCa)], with the chloride *trans* to the imine moiety, shows a resonance for H⁶, which is shifted down field by approximately 0.5 ppm with respect to that of H⁶ in the *trans,cis*-[Ru(Cl)₂(CO)₂(R-PyCa)] complex.^[42] This shift is not found for *cis,cis*-[Ru(I)(Me)(CO)₂(dmb)], and these signals are accordingly assigned to the latter conformation, with the methyl in an equatorial and the iodide in an axial position.

The complexes of the asymmetric ligand *i*Pr-PyCa can in principle form two diastereoisomers (Figure 5), both con-

Figure 5. General molecular structures of the diastereoisomers of *cis,cis*-[Ru(I)(Me)(CO)₂(iPr-PyCa)]



sisting of two enantiomers. ¹H- and ¹³C-NMR data reveal that only one diastereoisomer of *cis,cis*-[Ru(I)(Me)(CO)₂(iPr-PyCa)] is formed, since only one set of resonances is observed for the pyridine and imine moieties of the iPr-PyCa ligand. This diastereoisomer is proposed to have structure **a** (see Figure 5) with a carbonyl ligand *trans* to the strongly σ-donating and weakly π-accepting pyridine moiety and the methyl *trans* to the more weakly σ-donating and more strongly π-accepting imine part of the iPr-PyCa ligand. A similar structure had been found for *cis,cis*-[Ru(Cl)₂(CO)₂(R-PyCa)], which has the chloride in a *trans* position with respect to the imine moiety.^[42] Based on the ¹H- and ¹³C-NMR data alone, it is not possible to assign the position of the halide ligand. In order to confirm this proposal and prove the structure, an NOE-difference experiment was performed. These spectra show that an interaction exists between the methyl ligand and H⁶ of the pyridine moiety. Thus, the methyl ligand coordinates selectively *trans* with respect to the imine group, which confirms that the complex has the structure (**a**) of Figure 5.

It has been shown above that replacement of the methyl ligand by CO has hardly any influence on the NMR resonances of the *trans*-positioned α-diimine ligand. In contrast with this, changing the position of the methyl ligand from axial (*trans* to I[−]) to equatorial (*trans* to the α-diimine) on going from the *trans,cis* isomer to the *cis,cis* isomer, has a pronounced effect on the NMR signals of the methyl group. The methyl signals of the *cis,cis* complexes are observed in the region δ = 0.78–0.93, and those of the *trans,cis* complexes in the region δ = 0.08–0.10 (¹H NMR).^{[40][41]} This shift is most probably due to through-space interaction between the methyl and the iodide, when these ligands are in a *cis* position.^[42]

Electronic Absorption Spectra

The absorption spectral data of the complexes are collected in Table 3. Figure 6 (left) presents the spectra of the complexes *cis,cis*-[Ru(I)(Me)(CO)₂(L)] (L = dmb, iPr-PyCa, and iPr-DAB) in toluene. For comparison the spectra of both *trans,cis*- and *cis,cis*-[Ru(I)(Me)(CO)₂(iPr-DAB)] in toluene are depicted in Figure 6 (right).

In a previous article it was shown that the *trans,cis*-[Ru(X)(Me)(CO)₂(α-diimine)] (X = halide) complexes possess two visible absorption bands, the relative intensities of which depend on the halide used.^[51] In accordance with a similar behaviour observed for the corresponding *fac*- and *mer*-[Mn(X)(CO)₃(bpy)] complexes^[36], these two bands were then assigned to charge transfer transitions to the α-diimine ligand from two sets of orbitals having metal

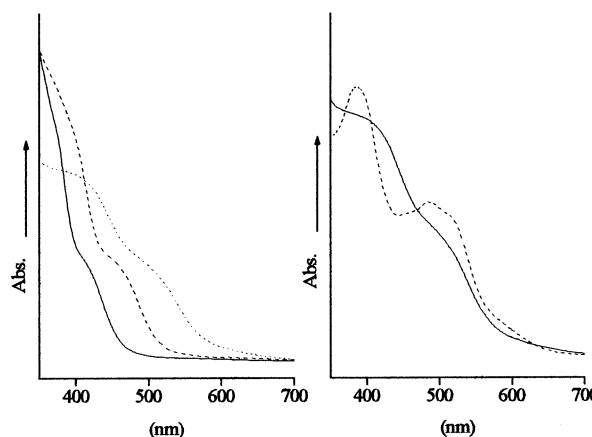
(d_π)–halide (p_π) bonding and anti-bonding character, respectively. In the case of the iodide complexes one of the iodide p_π orbitals has the largest contribution to the HOMO and the lowest-energy transition of *trans,cis*-[Ru(I)(Me)(CO)₂(α-diimine)] has therefore predominant halide to α-diimine (XLCT) character. The transitions of the higher energy band have mainly MLCT character.^[51]

Table 3. Absorption maxima [nm] and solvatochromism [Δ is σ_{max}(MeCN) – σ_{max}(toluene) in cm^{−1}] of *trans,cis*- and *cis,cis*-[Ru(I)(Me)(CO)₂(α-diimine)]

Compound	λ _{max} (MeCN)	λ _{max} (THF)	λ _{max} (toluene)	Δ
<i>cis,cis</i> -[Ru(I)(Me)(CO) ₂ (dmb)]	384; 344	405; 363	416; 374	2003; 2331
<i>trans,cis</i> -[Ru(I)(Me)(CO) ₂ (dmb)]	372	397	410	2491
<i>cis,cis</i> -[Ru(I)(Me)(CO) ₂ (iPr-PyCa)]	420; 378	438; 394	470; 403	2533; 1641
<i>trans,cis</i> -[Ru(I)(Me)(CO) ₂ (iPr-PyCa)] ^[a]		427; 350		
<i>cis,cis</i> -[Ru(I)(Me)(CO) ₂ (iPr-DAB)]	460; 383	478; 395	505; 416	1937; 2071
<i>trans,cis</i> -[Ru(I)(Me)(CO) ₂ (iPr-DAB)] ^[a]	436; 360	463; 374	485; 386	2320; 1870

[a] From ref. [51].

Figure 6. Left: Electronic absorption spectra of *cis,cis*-[Ru(I)(Me)(CO)₂(α-diimine)] (dmb = —, iPr-PyCa = ---- and iPr-DAB =) in toluene; right: electronic absorption spectra of *trans,cis*- (-----) and *cis,cis*-[Ru(I)(Me)(CO)₂(iPr-DAB)] (—) in toluene



A similar two-band system is observed in the spectra of the complexes *cis,cis*-[Ru(Me)(I)(CO)₂(α-diimine)]. Varying the α-diimine ligand from iPr-DAB to iPr-PyCa and dmb causes a shift of both absorption bands to higher energy (Figure 6). The shifts are closely related to the changes in energy of the lowest π* orbital of the α-diimine ligand.^{[15][52]} In the case of the dmb complex these shifts are so large, that the second absorption band has almost completely disappeared under the much stronger absorptions at higher energy. In agreement with its CT character, the lowest-energy band is solvatochromic, shifting to lower energy

by ca. 2000 cm^{-1} on going from acetonitrile to toluene (Table 3).

Resonance Raman Spectra

Resonance Raman (rR) spectroscopy is a very valuable technique for the assignment and characterisation of allowed electronic transitions.^{[53][54][55][56]} Since only those vibrations are normally resonance-enhanced, which are vibrationally coupled to the electronic transitions, these transitions can be characterised by the observed resonance effects. From the three *cis,cis* isomers rR spectra could only be recorded for the *cis,cis*-[Ru(I)(Me)(CO)₂(iPr-DAB)] and *cis,cis*-[Ru(I)(Me)(CO)₂(iPr-PyCa)] complexes. The corresponding dmb complex is too photolabile to provide reliable spectra. Spectra were obtained by excitation with the 488.0-nm line of an argon ion laser into the lowest-energy absorption band of the complexes. The resonantly enhanced Raman bands of the complexes are collected in Table 4. Figure 7 shows the rR spectra of *trans,cis*-[Ru(I)(R)(CO)₂(iPr-DAB)] (R = CD₃, CH₃) and *cis,cis*-[Ru(I)(CH₃)(CO)₂(α -diimine)] (α -diimine = iPr-DAB, iPr-PyCa), respectively. The spectra of *trans,cis*-[Ru(I)(R)(CO)₂(iPr-DAB)] (R = CD₃, CH₃) show a strong rR effect for a band at approximately 1555 cm^{-1} , which belongs to $\nu_s(\text{CN})$, the symmetrical stretching mode of the imine groups of the iPr-DAB ligand. This band is split in the rR spectra of the *cis,cis* isomer, indicating that the two imine groups of the iPr-DAB ligand are inequivalent due to the different *trans* influences of the Me and CO groups. This effect is not evident from the X-ray structures, but is also observed in the ¹H- and ¹³C-NMR spectra (vide supra). The Raman spectrum of *cis,cis*-[Ru(I)(Me)(CO)₂(iPr-PyCa)] is very similar to that of its *trans,cis* isomer.^[51]

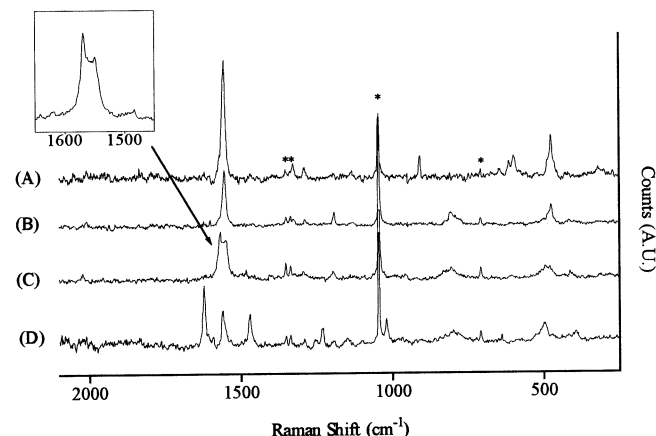
Table 4. Resonantly enhanced Raman bands of *trans,cis*- and *cis,cis*-[Ru(I)(R)(CO)₂(α -diimine)] (R = CH₃, CD₃; α -diimine = iPr-DAB, iPr-PyCa), measured at 80 K in KNO₃ + ft parenthesis λ_{exc} = 488.0 nm)

Compound	Raman shift [cm^{-1}]
<i>trans,cis</i> -[Ru(I)(CD ₃)(CO) ₂ (iPr-DAB)]	1555, 1328, 1287, 1132, 909, 615, 599, 475
<i>trans,cis</i> -[Ru(I)(Me)(CO) ₂ (iPr-DAB)]	2010, 1553, 1328, 1287, 1194, 806, 475
<i>cis,cis</i> -[Ru(I)(Me)(CO) ₂ (iPr-DAB)]	2022, 1568, 1550, 1293, 1198, 806, 486, 395
<i>cis,cis</i> -[Ru(I)(Me)(CO) ₂ (iPr-PyCa)]	1620, 1560, 1471, 1291, 1254, 1230, 1194, 1151, 1021, 801, 500, 395

The rather strong rR effect of $\nu_s(\text{CN})$ confirms the charge transfer character of the electronic transition in which excitation takes place. For both isomers there is hardly any rR effect for $\nu_s(\text{CO})$. This means that their charge transfer transitions do not originate from a central metal orbital since this would involve a change of metal-to-CO π back-bonding and invoke an rR effect for $\nu_s(\text{CO})$. Instead, the transition takes place from an orbital having mainly halide character just as for the *trans,cis* isomer.^[51] In addition, the rR spectra of *trans,cis*- and *cis,cis*-[Ru(I)(Me)(CO)₂(iPr-DAB)] show weaker rR effects for bands at 1328, 1194, 806,

and 475 cm^{-1} . Replacement of CH₃ by CD₃ in the *trans,cis* isomer causes a shift of the 1194 cm^{-1} band to 909 cm^{-1} , while the 806 cm^{-1} band is both shifted and split, giving rise to two new bands at 615 and 599 cm^{-1} , respectively. The positions of the other bands are not affected.

Figure 7. Resonance Raman spectra of (A) *trans,cis*-[Ru(I)(CD₃)(CO)₂(iPr-DAB)], (B) *trans,cis*-[Ru(I)(Me)(CO)₂(iPr-DAB)], (C) *cis,cis*-[Ru(I)(Me)(CO)₂(iPr-DAB)], (D) *cis,cis*-[Ru(I)(Me)(CO)₂(iPr-PyCa)] in KNO₃ at 80 K, λ_{exc} = 488.0 nm (* = NO₃⁻)



In agreement with the vibrational spectra of [M(CH₃)(CO)₅] and [M(CD₃)(CO)₅] (M = Mn, Re)^[57], the bands at 1194/909 cm^{-1} are assigned to $\delta_s(\text{CH}_3/\text{CD}_3)$ and those at 806/615;599 cm^{-1} to $\rho(\text{CH}_3/\text{CD}_3)$. The doublet spacing of the $\rho(\text{CD}_3)$ band in [Ru(I)(CD₃)(CO)₂(iPr-DAB)] (16 cm^{-1}) is rather small compared with that observed for [Re(CH₃)(CO)₅] (44 cm^{-1})^[57] and [Re(CD₃)(CO)₃(dmb)] (51 cm^{-1}).^[58] The rR effect of the two methyl vibrations is clearly an electronic effect and not the result of a coupling to other vibrations since the deuteration does not affect the frequencies of other Raman bands. The observation of these CH₃/CD₃ bands implies that the charge transfer transition influences the bond angles of these ligands, most probably as a result of a change of the hybridisation of the C atom of the CH₃ ligand due to a charge redistribution during the charge transfer transition.

The observation that deuteration of the methyl ligand does not affect the frequency of any Raman bands below 800 cm^{-1} , leads to the following conclusions. First of all, the Raman band at approximately 500 cm^{-1} does not belong to $\nu(\text{Ru}-\text{CH}_3)$ and is assigned to $\nu_s(\text{Ru}-\text{CO})$, expected in this frequency region. Secondly, the absence of a rR effect for $\nu(\text{Ru}-\text{CH}_3)$ implies that the electronic transition, in which the excitation takes place, does not influence the Ru-methyl σ bond, although it affects the bond angles of the methyl ligand. This result agrees with the proposed XLCT character of the transition and excludes the possibility that the lowest-energy absorption band belongs to an allowed $\sigma(\text{Ru-methyl}) \rightarrow \pi^*(\alpha\text{-diimine})$ transition instead.

According to the rR spectra, the *trans,cis* and *cis,cis* isomers of the [Ru(I)(Me)(CO)₂(iPr-DAB)] complexes have very similar low-energy transitions. The difference in photo-

chemistry between *trans,cis*- and *cis,cis*-[Ru(I)(Me)(CO)₂(dmb)], viz. photoisomerization of the *trans,cis* into the *cis,cis* isomer and no apparent product formation of the *cis,cis* isomer, can therefore not be ascribed to a different character of the lowest excited state. This difference in photochemical behaviour is the subject of a detailed photochemical study of these complexes, the results of which will be published in a forthcoming article.

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Experimental Section

Materials, Apparatus and Preparations: [Ru₃(CO)₁₂], MeI, BzIbR, silver triflate (AgOTf), (nBu)₄NI, and 4,4'-dimethyl-2,2'-bipyridine (dmb) were used without further purification. Silica gel for column chromatography (Kieselgel 60, 70–230 mesh, Merck) was activated by heating overnight in vacuo at 160°C. Solvents for synthetic purposes were of reagent grade and carefully dried over sodium wire (THF, *n*-hexane, diethyl ether) or CaCl₂ (CH₂Cl₂) and freshly distilled under nitrogen prior to use. Acetonitrile was used without further purification. Solvents for spectroscopic measurements were of analytical grade, dried over sodium and distilled under N₂ before use. *i*Pr-DAB and *i*Pr-PyCa were synthesised according to literature procedures.^[59] Electronic absorption spectra were measured with a Varian Cary 4E spectrophotometer, infrared spectra with an FTS-60A FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. – The ¹H-, NOE-difference, and ¹³C-NMR spectra were recorded with a Bruker AMX 300 spectrometer (300.13, 75.46 MHz, respectively) at 293K. Resonance Raman measurements were performed with a Dilor XY spectrometer, using an SP Model 2016 argon ion laser as excitation source. To avoid photodecomposition the spectra of the complexes (dispersed in a KNO₃ pellet) were measured at 80K. Typical concentrations were 30 mg of complex and 150 mg of KNO₃.

Synthesis of *cis,cis*-[Ru(I)(Me)(CO)₂(L)] (L = *i*Pr-DAB, *i*Pr-PyCa, dmb): Ru₃(CO)₁₂ (300 mg, 0.46 mmol) and MeI (1.5 ml, excess) were refluxed in 20 ml of acetonitrile at 100°C. After 10 min, a product with CO-stretching frequencies at 2058 (s), 1996 (s) and 1637 (w) was obtained. The reaction was brought to completion within ca. 1 h; a yellow solution was then obtained which contained product **2a** with CO-stretching frequencies of 2041 (s) and 1974 (s) cm⁻¹. After evaporating the solvent, product **2a** was dissolved in 10 ml of diethyl ether together with 0.5 mmol of the α-diimine ligand. After stirring for 1 h, the solution was filtered off and the residue was washed with hexane (2 × 10 ml). The complex was purified by column chromatography on silica gel using gradient elution with CH₂Cl₂/THF. Yield 80–90%.

cis,cis-[Ru(I)(Me)(CO)₂(*i*Pr-DAB)]: ¹H NMR (CDCl₃): δ = 8.26/8.20 (s, 1 H, H_{im}), 4.64/4.20 [sept, *J* = 6.6 Hz, 1 H, CH(CH₃)₂], 1.63/1.55/1.49/1.40 [d, *J* = 6.6 Hz, 3 H, CH(CH₃)₂], 0.78 (s, 3 H, Ru-Me). – ¹³C NMR APT (CDCl₃): δ = 200.8 (Ru-CO_{eq}), 193.3 (Ru-CO_{ax}), 160.1/157.7 (CH_{im}), 65.6/57.2 [CH(CH₃)₂], 24.8/23.5/23.3/22.2 [CH(CH₃)₂], –14.7 (Ru-CH₃). – IR (CH₂Cl₂): ν(CO) = 2028 (s), 1958 (s) cm⁻¹. – MS (FAB⁺): M(calcd.) 439.95, M(found) 439.95.

cis,cis-[Ru(I)(Me)(CO)₂(*i*Pr-PyCa)]: ¹H NMR (CDCl₃): δ = 9.01 (d, *J* = 5.1 Hz, 1 H, py-H⁶), 8.48 (s, 1 H, H_{im}), 8.05 (t, *J* =

7.7 Hz, 1 H, py-H⁴), 7.85 (d, *J* = 7.7 Hz, 1 H, py-H³), 7.61 (t, *J* = 5.1 Hz, 1 H, py-H⁵), 4.20 [sept, 6.3 Hz, 1 H, CH(CH₃)₂], 1.64/1.52 [d, 6.3 Hz, 6 H, CH(CH₃)₂], 0.93 (s, 3 H, Ru-Me). – ¹³C NMR APT (CDCl₃): δ = 201.1 (Ru-CO_{eq}), 194.0 (Ru-CO_{ax}), 160.2 (H_{im}), 155.5 (py-C²), 149.7 (py-C⁶), 138.8 (py-C³), 127.7 (py-C⁵), 126.6 (py-C⁴), 65.3 [CH(CH₃)₂], 24.6/23.7 [CH(CH₃)₂], –13.4 (Ru-CH₃). – IR (CH₂Cl₂): ν(CO) = 2027 (s), 1956 (s) cm⁻¹. – MS (FAB⁺): M(calcd.) 449.92, M(found) 449.92.

cis,cis-[Ru(I)(Me)(CO)₂(dmb)]: ¹H NMR (CDCl₃): δ = 8.85 (d, *J* = 5.6 Hz, 2 H, py-H⁶), 7.99/7.96 (s, 2 H, py-H³/py-H^{3'}), 7.38/7.27 (d, *J* = 5.6 Hz, 1 H, py-H⁵/py-H^{5'}), 2.58/2.55 (s, 6 H, py-Me/py-Me'), 0.89 (s, 3 H, Ru-Me). – ¹³C NMR APT (CDCl₃): δ = 200.7 (Ru-CO_{eq}), 195.6 (Ru-CO_{ax}), 156.0/153.5 (py-C²/py-C^{2'}), 153.0/148.8 (py-C⁶/py-C^{6'}), 150.2/149.8 (py-C⁴/py-C^{4'}), 127.1/126.7 (py-C³/py-C^{3'}), 123.4/123.2 (py-C⁵/py-C^{5'}), 21.2 (py-CH₃), –14.3 (Ru-CH₃). – IR (CH₂Cl₂): ν(CO) = 2025 (s), 1952 (s) cm⁻¹. – MS (FAB⁺): M(calcd.) 483.92, M(found) 483.92.

Synthesis of *trans,cis*-[Ru(I)(Me)(CO)₂(L)] (L = *i*Pr-DAB, dmb): The complexes *trans,cis*-[Ru(I)(R)(CO)₂(*i*Pr-DAB)] (R = CH₃, CD₃), which were used for X-ray structure analysis and Raman spectroscopic measurements, were prepared by the procedure described by Kraakman et al.^[40] The corresponding dmb complex was prepared from its *cis,cis* isomer according to the following procedure. One equivalent of AgOTf was added to a solution of *cis,cis*-[Ru(I)(Me)(CO)₂(dmb)] in CH₂Cl₂, which was then stirred for 2 h. The residue, AgI, was filtered off and 1 g (excess) of (nBu)₄NI was added while light was excluded to prevent photodecomposition. This solution was stirred for 3 h. The excess of (nBu)₄NI and (nBu)₄NOTf was filtered off and the solvent was evaporated. The complex was purified by column chromatography on silica gel using gradient elution with CH₂Cl₂/THF. Yield 80–90%.

trans,cis-[Ru(I)(Me)(CO)₂(dmb)]: ¹H NMR (CDCl₃): δ = 8.83 (d, *J* = 5.7 Hz, 2 H, py-H⁶), 7.96 (s, 2 H, py-H³), 7.30 (d, *J* = 5.7 Hz, 2 H, py-H⁵), 2.56 (s, 6 H, py-Me), 0.10 (s, 3 H, Ru-Me). – ¹³C NMR APT (CDCl₃): δ = 202.2 (Ru-CO), 153.4 (py-C²), 151.6 (py-C⁶), 150.2 (py-C⁴), 127.2 (py-C³), 123.5 (py-C⁵), 21.3 (py-CH₃), –4.8 (Ru-CH₃). – IR (CH₂Cl₂): ν(CO) = 2030 (s), 1962 (s) cm⁻¹.

Synthesis of *cis,cis*-[Ru(I){C(O)Me}(CO)₂(*i*Pr-DAB)]: Ru₃(CO)₁₂ (300 mg, 0.46 mmol) and MeI (1.5 ml, excess) were refluxed in 20 ml of acetonitrile at 100°C. The reaction was completed after ca. 1 h; a yellow solution was then obtained containing product **2a** with ν(CO) frequencies of 2041(s) and 1974(s) cm⁻¹. The solution was pressurised with CO (1 atm) and stirred for 2 h. Product **1a** was obtained with ν(CO) of 2058(s) and 1996(s) cm⁻¹. After evaporation of the solvent, product **1a** and 75 mg (0.5 mmol) of *i*Pr-DAB were dissolved in 10 ml of diethyl ether. After stirring for 1 h, the solution was filtered and the residue was washed with hexane (2 × 10 ml). The complex was purified by column chromatography on silica gel using gradient elution with CH₂Cl₂/THF. Total yield 75% {the ¹H-NMR spectrum shows that *trans,cis*-[Ru(I){C(O)Me}(CO)₂(*i*Pr-DAB)] and *cis,cis*-[Ru(I){C(O)Me}(CO)₂(*i*Pr-DAB)] are formed in a 1:4 ratio}.

trans,cis-[Ru(I){C(O)Me}(CO)₂(*i*Pr-DAB)]: ¹H NMR (CDCl₃): δ = 8.20 (s, 2 H, H_{im}), 4.24 [sept, *J* = 6.6 Hz, 2 H, CH(CH₃)₂], 2.53 [s, 3 H, Ru-C(O)Me], 1.43/1.38 [d, *J* = 6.6 Hz, 6 H, CH(CH₃)₂]. – IR (CH₂Cl₂): ν(CO) = 2040 (s), 1974 (s), 1640 (w) cm⁻¹.

cis,cis-[Ru(I){C(O)Me}(CO)₂(*i*Pr-DAB)]: ¹H NMR (CDCl₃): δ = 8.20/8.18 (1 H, s, H_{im}), 5.15/4.17 [sept, *J* = 6.6 Hz, 2 H, CH(CH₃)₂], 2.81 [s, 3 H, Ru-C(O)Me], 1.69–1.38 [m, *J* = 6.6 Hz, 12 H, CH(CH₃)₂]. – IR (CH₂Cl₂): ν(CO) = 2040 (s), 1974 (s), 1640 (w) cm⁻¹.

Synthesis of Product 2b: $\text{Ru}_3(\text{CO})_{12}$ (300 mg, 0.46 mmol) and $\text{BzI}Br$ (0.5 ml, excess) were refluxed in 20 ml of acetonitrile at 100°C. After completion of the reaction (ca. 0.5 h), a yellow solution was obtained with product **2b** having $\nu(\text{CO})$ frequencies of 2042(s) and 1976(s) cm^{-1} and a product with $\nu(\text{CO})$ bands at 2077(s) and 2020(s), in a 2:1 ratio. After evaporation of the solvent, the complex was washed with diethyl ether (2×10 ml). Yield 30%.

Product 2b: ^1H NMR (CDCl_3): $\delta = 7.25\text{--}7.15$ (m, 4 H, H_{Ph}), 7.01 (m, 1 H, H_{Ph}), 2.96/2.89 (d, $^2J = 8.5$ Hz, 2 H, PhCH_2), 2.29/2.26 (s, 3 H, CH_3CN). – IR (MeCN): $\nu(\text{CO}) = 2042$ (s), 1976 (s) cm^{-1} .

Synthesis of *cis,cis*-[Ru(*Br*)(*BzI*)(*CO*)₂(*iPr-DyAB*)]: Product **2b** was prepared in acetonitrile. After evaporation of the solvent, complex **2b** and 0.5 mmol of *iPr-DAB* were dissolved in 10 ml of diethyl ether. After stirring for 0.5 h, the solution was filtered off and the residue was washed with hexane (2×10 ml). Yield 50%.

***cis,cis*-[Ru(*Br*)(*BzI*)(*CO*)₂(*iPr-DAB*)]:** ^1H NMR (CDCl_3): $\delta = 8.26/8.24$ (s, 1 H, H_{im}), 7.37 (d, $J = 7.5$ Hz, 2 H, H_{Ph}), 7.17 (t, $J = 7.5$ Hz, 2 H, H_{Ph}), 6.95 (t, $J = 7.5$ Hz, 1 H, H_{Ph}), 4.64/4.11 [sept, $J = 6.6$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.57 (d, $^2J = 7.8$ Hz, 1 H, PhCH_2), 2.98 (d, $^2J = 7.8$ Hz, 1 H, PhCH_2), 1.56–1.41 [m, 12 H, $\text{CH}(\text{CH}_3)_2$]. – IR (CH_2Cl_2): $\nu(\text{CO}) = 2030$ (s), 1962 (s) cm^{-1} .

Synthesis of *trans,cis*-[Ru(*Br*)(*BzI*)(*CO*)₂(*iPr-DAB*)]: This complex was prepared by the procedure of Kraakman et al.^[40]

***trans,cis*-[Ru(*Br*)(*BzI*)(*CO*)₂(*iPr-DAB*)]:** ^1H NMR (CDCl_3): $\delta = 8.16$ (s, 2 H, H_{im}), 7.10 (t, $J = 7.6$ Hz, 2 H, H_{Ph}), 7.02 (t, $J = 7.5$ Hz, 1 H, H_{Ph}), 6.88 (d, $J = 7.5$ Hz, 2 H, H_{Ph}), 4.22 [sept, $J = 6.6$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$], 2.36 (s, 2 H, PhCH_2), 1.61/1.38 [d, 12 H, $\text{CH}(\text{CH}_3)_2$]. – IR (CH_2Cl_2): $\nu(\text{CO}) = 2033$ (s), 1969 (s) cm^{-1} .

Crystal Structure Determination of *trans,cis*-[Ru(*I*)(*Me*)(*CO*)₂(*iPr-DAB*)] and *cis,cis*-[Ru(*I*)(*Me*)(*CO*)₂(*iPr-DAB*)]: Crystals of both compounds were grown from a saturated CH_2Cl_2 solution at 293 K. Crystals with approximate dimensions $0.20 \times 0.30 \times 0.40$ mm ($0.15 \times 0.20 \times 0.60$ mm) were used for data collection with an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation and ω -2 θ scan. Totals of 4661 (4819) unique reflections were measured. Of these, 3168 (1931) were above the significance level of $2.5 \sigma(I)$. The maximum value of $(\sin \theta)/\lambda$ was $0.70 \text{ \AA}^{-1}$. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $40^\circ < 2\theta < 41^\circ$ ($40^\circ < 2\theta < 42^\circ$). Corrections for Lorentz and polarization effects were applied. The structures were solved by the PATTY option of the DIRDIF-94 program system.^[60] Hydrogen atom positions were calculated. Full-matrix least-squares refinement of F , anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, with a fixed temperature factor of $U = 0.15 \text{ \AA}^2$ and restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.0 Å, converged to $R = 0.043$ (0.065), $R_w = 0.045$ (0.063), $(\Delta \sigma)_{\text{max}} = 0.45$ (0.61), $S = 0.81$ (1.49). An empirical absorption correction (DIFABS^[61]) was applied, with coefficients in the range of 0.68–1.22 (0.40–1.53). A final difference Fourier map revealed a residual electron density between -0.7 and $0.7 \text{ e\AA}^{-3}$ (-1.2 and $1.0 \text{ e\AA}^{-3}$) in the vicinity of the heavy atoms. Scattering factors were taken from Cromer and Mann.^{[62][63]} The anomalous scattering of Ru and I was taken into account.^[64] All calculations were performed with XTAL^[65], unless stated otherwise. Both isomers were refined in the same way but after isotropic refinement of the starting model of the *cis,cis* isomer some atoms had a rather high temperature factor (C5, C8 and O9). C5 and C8 could be split into two positions a and b with occupancy factors for a = 0.35 and for b = 0.65. O9 was divided in such a way that the

CO and CH_3 were both equally distributed over the two possible positions and thus resulting in the introduction of two half occupied O positions (O9 and O11). The disordered C atoms were kept isotropic during refinement. No attempts were made to calculate the H atoms for C5a, C5b, C8a and C8b and the H atoms for C3 and C6 were divided into separate positions and kept fixed entirely at their calculated position. The experimental data for the crystal structure determinations and refinements are listed in Table 5.

Table 5. Crystallographic data and details of the structure determinations of *trans,cis*-[Ru(*I*)(*Me*)(*CO*)₂(*iPr-DAB*)] (**A**) and *cis,cis*-[Ru(*I*)(*Me*)(*CO*)₂(*iPr-DAB*)] (**B**)

	A	B
<i>Crystal data</i>		
Chemical formula	$\text{C}_{11}\text{H}_{19}\text{IN}_2\text{O}_2\text{Ru}$	$\text{C}_{11}\text{H}_{19}\text{IN}_2\text{O}_2\text{Ru}$
Formula weight	439.3	439.3
Lattice type	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
a [Å]	7.389(2)	7.409(1)
b [Å]	22.880(3)	22.434(8)
c [Å]	10.540(2)	10.140(3)
β [°]	98.41(1)	99.31(2)
V [Å ³]	1608.7(6)	1663.2(9)
Crystal size [mm]	$0.20 \times 0.30 \times 0.40$	$0.15 \times 0.20 \times 0.60$
D_x [g cm ⁻³]	1.81	1.75
$F(000)$	848	848
μ (Mo- K_α) [cm ⁻¹]	28.5	27.57
<i>Data collection</i>		
T [K]	293	293
λ (Mo- K_α) [Å]	0.71069	0.71069
θ_{min} , θ_{max} [°]	2.0, 29.9	1.8, 29.9
Monochromator	graphite	graphite
$\Delta\omega$ [°]	$1.20 + 0.35 \tan \theta$	$1.30 + 0.35 \tan \theta$
Aperture [mm]	$3.0 + 1.0 \tan \theta$	$3.0 + 1.0 \tan \theta$
Exposure time [h]	65	60
Linear instability [%]	—	—
Reference reflections	121, 210	161, 122
Dataset	0/10, 0/29, $-14/14$	$-10/0$, 0/31, $-13/14$
Total unique data	4661	4819
Observed data	3168 ($I > 2.5\sigma_I$)	1931 ($I > 2.5\sigma_I$)
DIFABS	0.68–1.22	0.40–1.53
<i>Refinement</i>		
R	0.043	0.065
R_w	0.045	0.063
w^{-1}	$6.0 + 0.012[\sigma(F_o)]^2$	$4.0 + 0.015[\sigma(F_o)]^2$
$(\Delta/\sigma)_{\text{max}}$	0.45	0.61
Min., max. resd. dens.	$-0.7, 0.7$	$-1.2, 1.0$
[eÅ ³]		

[1] K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, 46, 159.

[2] R. J. Watts, *J. Chem. Educ.* **1983**, 60, 834.

[3] H. Riesen, Y. Gao, E. Krausz, *Chem. Phys. Lett.* **1994**, 228, 610.

[4] D. J. Stufkens, *Comments Inorg. Chem.* **1992**, 13, 359.

[5] T. A. Perkins, W. Humer, T. L. Netzel, K. S. Schanze, *J. Phys. Chem.* **1990**, 94, 2229.

[6] P. Chen, T. D. Westmoreland, E. Danielson, K. S. Schanze, D. Anthon, P. E. Neveux, Jr., T. J. Meyer, *Inorg. Chem.* **1987**, 26, 1116.

[7] K. S. Schanze, D. B. MacQueen, T. A. Perkins, L. A. Cabana, *Coord. Chem. Rev.* **1993**, 122, 63.

[8] L. A. Worl, R. Duesing, P. Chen, L. D. Ciana, T. J. Meyer, *J. Chem. Soc., Dalton Trans.* **1991**, 849.

[9] J. C. Luong, R. A. Faltynek, M. S. Wrighton, *J. Am. Chem. Soc.* **1980**, 102, 7892.

[10] J. C. Luong, R. A. Faltynek, M. S. Wrighton, *J. Am. Chem. Soc.* **1979**, 101, 1597.

[11] D. L. Morse, M. S. Wrighton, *J. Am. Chem. Soc.* **1976**, 98, 3931.

[12] M. W. Kokkes, D. J. Stufkens, A. Oskam, *Inorg. Chem.* **1985**, 24, 2934.

[13] M. W. Kokkes, W. G. J. de Lange, D. J. Stufkens, A. Oskam, *J. Organomet. Chem.* **1985**, 294, 59.

- [14] M. W. Kokkes, D. J. Stufkens, A. Oskam, *Inorg. Chem.* **1985**, *24*, 4411.
- [15] D. J. Stufkens, *Coord. Chem. Rev.* **1990**, *104*, 39.
- [16] R. R. Andréa, W. G. J. de Lange, D. J. Stufkens, A. Oskam, *Inorg. Chem.* **1989**, *28*, 318.
- [17] H. K. van Dijk, J. van der Haar, D. J. Stufkens, A. Oskam, *Inorg. Chem.* **1989**, *28*, 75.
- [18] T. van der Graaf, D. J. Stufkens, A. Oskam, K. Goubitz, *Inorg. Chem.* **1991**, *30*, 599.
- [19] T. van der Graaf, A. van Rooy, D. J. Stufkens, A. Oskam, *Inorg. Chim. Acta* **1991**, *187*, 133.
- [20] J. W. M. van Outersterp, D. J. Stufkens, A. Vlček, Jr., *Inorg. Chem.* **1995**, *34*, 5183.
- [21] B. D. Rossenaar, T. van der Graaf, R. van Eldik, C. H. Langford, D. J. Stufkens, A. Vlček, Jr., *Inorg. Chem.* **1994**, *33*, 2865.
- [22] B. D. Rossenaar, E. Lindsay, D. J. Stufkens, A. Vlček, Jr., *Inorg. Chim. Acta* **1996**, *250*, 5.
- [23] P. C. Servaas, G. J. Stor, D. J. Stufkens, A. Oskam, *Inorg. Chim. Acta* **1990**, *178*, 185.
- [24] H. A. Nieuwenhuis, A. van Loon, M. A. Moraal, D. J. Stufkens, A. Oskam, K. Goubitz, *J. Organomet. Chem.* **1995**, *492*, 165.
- [25] M. P. Aarnts, D. J. Stufkens, A. Vlček, Jr., *Inorg. Chim. Acta*, **1997**, *226*, 37.
- [26] M. P. Aarnts, D. J. Stufkens, M. P. Wilms, E. J. Baerends, A. Vlček, Jr., I. P. Clark, M. W. George, J. J. Turner, *Chem. Eur. J.* **1996**, *2*, 1556.
- [27] B. D. Rossenaar, C. J. Kleverlaan, M. C. E. van de Ven, D. J. Stufkens, A. Vlček, Jr., *Chem. Eur. J.* **1996**, *2*, 228.
- [28] B. D. Rossenaar, D. J. Stufkens, A. Oskam, J. Fraanje, K. Goubitz, *Inorg. Chim. Acta* **1996**, *247*, 215.
- [29] B. D. Rossenaar, C. J. Kleverlaan, M. C. E. van de Ven, D. J. Stufkens, A. Oskam, J. Fraanje, K. Goubitz, *J. Organomet. Chem.* **1995**, *493*, 153.
- [30] B. D. Rossenaar, M. W. George, F. P. A. Johnson, D. J. Stufkens, J. J. Turner, A. Vlček, Jr., *J. Am. Chem. Soc.* **1995**, *117*, 11582.
- [31] C. J. Kleverlaan, D. M. Martino, H. v. Willigen, D. J. Stufkens, A. Oskam, *J. Phys. Chem.* **1996**, *100*, 18607.
- [32] H. A. Nieuwenhuis, M. C. E. van de Ven, D. J. Stufkens, A. Oskam, K. Goubitz, *Organometallics* **1995**, *14*, 780.
- [33] P. Bradley, G. Suardi, A. P. Zipp, R. Eisenberg, *J. Am. Chem. Soc.* **1994**, *116*, 2859.
- [34] J. E. Hux, R. J. Puddephat, *J. Organomet. Chem.* **1992**, *437*, 251.
- [35] K. Kaupp, H. Stoll, W. Kaim, T. Stahl, G. van Koten, E. Wising, W. J. Smeets, A. L. Spek, *J. Am. Chem. Soc.* **1991**, *113*, 5606.
- [36] G. J. Stor, S. L. Morrison, D. J. Stufkens, A. Oskam, *Organometallics* **1994**, *13*, 2641.
- [37] C. J. Kleverlaan, F. Hartl, D. J. Stufkens, *J. Photochem. Photobiol.* **1997**, *203*, 231.
- [38] W. Rohde, H. tom Dieck, *J. Organomet. Chem.* **1987**, *328*, 209.
- [39] H. tom Dieck, W. Rohde, U. Behrens, *Z. Naturforsch.* **1989**, *44b*, 158.
- [40] M. J. A. Kraakman, K. Vrieze, H. Kooijman, A. L. Spek, *Organometallics* **1992**, *11*, 3760.
- [41] B. de Klerk-Engels, J. H. Groen, J. M. A. Kraakman, J.-M. Ernsting, K. Vrieze, K. Goubitz, J. Fraanje, *Organometallics* **1994**, *13*, 3279.
- [42] B. de Klerk-Engels, H.-W. Frühauf, K. Vrieze, H. Kooijman, A. L. Spek, *Inorg. Chem.* **1993**, *32*, 5528.
- [43] M. J. A. Kraakman, B. de Klerk-Engels, P. P. M. de Lange, K. Vrieze, W. J. J. Smeets, A. L. Spek, *Organometallics* **1992**, *11*, 3774.
- [44] W. Rohde, H. tom Dieck, *J. Organomet. Chem.* **1990**, *385*, 101.
- [45] H. A. Nieuwenhuis, A. van Loon, M. A. Moraal, D. J. Stufkens, A. Oskam, K. Goubitz, *Inorg. Chim. Acta* **1995**, *232*, 19.
- [46] B. J. Rappoli, K. J. McGrath, C. F. George, J. C. Cooper, *J. Organomet. Chem.* **1993**, *450*, 85.
- [47] H. tom Dieck, W. Kollvitz, I. Kleinwachter, W. Rohde, L. Stamp, *Transition Met. Chem.* **1986**, *11*, 361.
- [48] J. M. A. Kraakman, K. Vrieze, H. Kooijman, A. L. Spek, *Organometallics* **1992**, *11*, 3774.
- [49] J.-C. Daran, Y. Jeannin, C. Rigault, *Acta Crystallogr.* **1984**, *C40*, 249.
- [50] E. Alessio, B. Milani, M. Bolle, G. Mestroni, P. Faleschini, F. Tonone, S. Geremia, M. Calligaris, *Inorg. Chem.* **1995**, *34*, 4722.
- [51] H. A. Nieuwenhuis, D. J. Stufkens, A. Oskam, *Inorg. Chem.* **1994**, *33*, 3212.
- [52] J. Reinhold, R. Benedix, P. Birner, H. H., *Inorg. Chim. Acta* **1979**, *33*, 209.
- [53] R. J. H. Clark, T. J. Dines, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 131.
- [54] J. I. Zink, K.-S. Kim Shin, *Adv. Photochem.* **1991**, *16*, 119.
- [55] R. W. Balk, D. J. Stufkens, A. Oskam, *J. Chem. Soc., Dalton Trans.* **1981**, 1124.
- [56] R. W. Balk, T. Snoeck, D. J. Stufkens, A. Oskam, *Inorg. Chem.* **1980**, *19*, 3015.
- [57] G. P. McQuillan, D. C. McKean, C. Long, A. R. Morrisson, I. Torto, *J. Am. Chem. Soc.* **1986**, *108*, 863.
- [58] C. J. Kleverlaan, D. J. Stufkens, *Inorg. Chim. Acta*, in press.
- [59] H. Bock, H. tom Dieck, *Chem. Ber.* **1967**, *100*, 228.
- [60] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *The DIRDIF-94 program system*, University of Nijmegen, Netherlands, **1994**.
- [61] N. Walker, D. Stuart, *Acta Crystallogr.* **1983**, *A39*, 158.
- [62] *International Tables for X-Ray Crystallography* Birmingham, Kynoch Press, **1974**, vol. IV, p. 55.
- [63] D. T. Cromer, J. B. Mann, *Acta Crystallogr.* **1986**, *A24*, 321.
- [64] D. T. Cromer, J. B. Liberman, *J. Chem. Phys.* **1970**, *53*, 1891.
- [65] S. R. Hall, H. D. Flack, J. M. Stewart, *Eds. XTAL3.2 Reference Manual, Universities of Western Australia, Geneva and Maryland*, **1992**.

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