Synthesis and Spectroscopic Properties of CpRuCl(R-DAB(4e)) and $CpRuCo(CO)_3$(R-DAB(6e)). Part XVII. X-ray Structure Determination of $CpRuCo(CO)_3$(t-Bu-DAB(6e))*

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Abstract

$CpRuCl(PPh_3)_2$ reacted with excess R-DAB† in refluxing toluene to give CpRuCl(R-DAB(4e)) (**1a**: R = i-Pr; **1b**: R = t-Bu; **1c**: R = neo-Pent; **1d**: R = *p*-Tol). ^1H NMR and ^{13}C NMR spectroscopic data indicated that in these complexes the R-DAB ligand is bonded in a chelating 4e coordination mode.

Reaction of **1a** and **1b** with one equivalent of $[Co(CO)_4]^-$ afforded $CpRuCo(CO)_3$(R-DAB(6e)) (**2a**: R = i-Pr; **2b**: R = t-Bu). The structure of **2b** was determined by a single crystal X-ray structure determination. Crystals of **2b** are monoclinic, space group $P2_1/n$, with four molecules in a unit cell of dimensions: $a = 16.812(4)$, $b = 12.233(3)$, $c = 9.938(3)$ Å and $\beta = 105.47(3)°$. The structure was solved via the heavy atom method and refined to $R = 0.060$ and $R_w = 0.065$ for the 3706 observed reflections. The molecule contains a Ru–Co bond of 2.660(3) Å and a cyclopentadienyl group that is η^5-coordinated to ruthenium [Ru–C(cyclopentadienyl) = 2.208(3) Å (mean)]. Two carbonyls are terminally coordinated to cobalt (Co–C(1) = 1.746(7) and Co–C(2) = 1.715(6) Å) while the third is slightly asymmetrically bridging the Ru–Co bond (Ru–C(3) = 2.025(6) and Co–C(3) = 1.912(6) Å). The Ru–C(3)–O(3) and Co–C(3)–O(3) angles are 138.4(5)° and 136.5(5)°, respectively. The t-Bu-DAB ligand is in the bridging 6e coordination mode: σ-N coordinated to Ru (Ru–N(2) = 2.125(4) Å), μ_2-N′ bridging the Ru–Co bond and η^2-C=N coordinated to Co (Ru–N(1) = 2.113(5), Co–N(1) = 1.941(4) and Co–C(4) = 2.084(5) Å). The η^2-C=N′ bonded imine group has a bond length of 1.394(7) Å indicating substantial π-backbonding from Co into the antibonding orbital of this C=N bond.

^1H NMR spectroscopy indicated that **2a** and **2b** are fluxional on the NMR time scale. The fluxionality of 6e bonded R-DAB ligands is rarely observed and may be explained by the reversible interchange of the σ-N and η^2-C=N′ coordinated imine parts of the R-DAB ligand.

Introduction

In our laboratory research has been focused on the influence of the versatile R-DAB and R-Pyca ligands on the formation of polynuclear metal–metal bonded carbonyl complexes [2a–c].

From the outset we have utilized nucleophilic substitution reactions for the preparation of homo- and heteronuclear metal–metal bonded complexes. However, it has been found that $MnX(CO)_3$(R-DAB(4e)) (X = Cl, Br) for example may react in various ways with nucleophiles. Reactions of $MnX(CO)_3$(R-DAB(4e)) with $[Mn(CO)_5]^-$ and with $[Co(CO)_4]^-$ afforded $Mn(CO)_3$(R-DAB(4e))$Mn(CO)_5$ ($Mn_2(CO)_8$(R-DAB(4e)); see Fig. 1a), with a σ,σ-N,N′ coordinated R-DAB ligand and $MnCo(CO)_6$(R-DAB(6e)) (Fig. 1b), with a σ-N,μ_2-N′,η^2-C=N′ coordinated R-DAB ligand respectively [3, 4]. The possibility of the R-DAB ligand to change its bonding from 4e to 6e coordination mode was nicely demonstrated by the photochemical interconversion between $Mn_2(CO)_8$(R-Pyca(4e)) and $Mn_2(CO)_7$(R-Pyca(6e)) as well as between $Fe_2(CO)_7$(R-Pyca(4e)) and $Fe_2(CO)_6$(R-Pyca(6e)) [5a, b]. On the other hand the reaction of $MnX(CO)_3$(R-DAB(4e)) with

*For Parts XV and XVI see ref. 1.

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†1,4-Disubstituted-1,4-diaza-1,3-butadienes, R–N=C(R^1)–C(R^2)=N–R, are abbreviated as R-DAB{R^1,R^2}. When R^1 = R^2 = H the abbreviation R-DAB can be used. Pyridine-2-carbaldimines, C_5H_4N-2-C(H)=N–R, are abbreviated as R-Pyca. The number of electrons donated by the α-diimine ligand to the cluster is indicated between brackets, *i.e.* R-DAB(4e) stands for σ,σ-N,N′ chelating 4e coordinated; R-DAB(6e) stands for σ-N,μ_2-N′,η^2-C=N′ bridging 6e coordinated; R-DAB(8e) stands for σ,σ-N,N′-η^2,η^2-C=N,C′=N′ bridging 8e coordinated.

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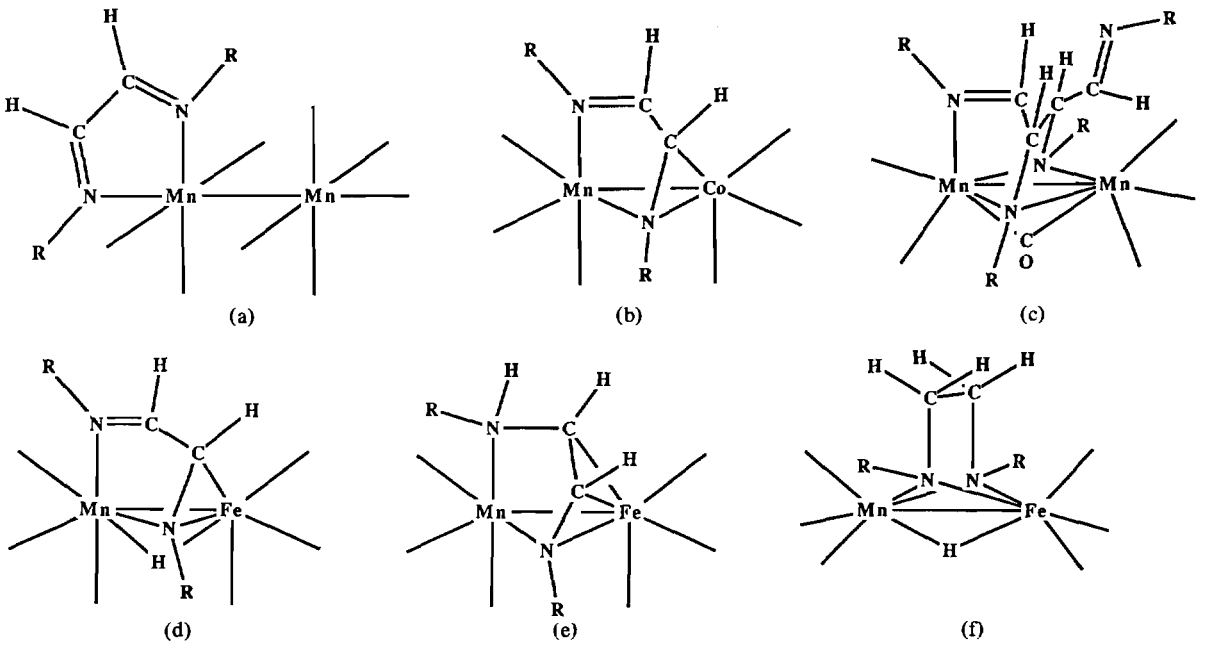


Fig. 1. Schematic structures of (a) $Mn(CO)_3$(R-DAB(4e))$Mn(CO)_5$, (b) $MnCo(CO)_6$(R-DAB(6e)), (c) $Mn_2(CO)_6$(R-IAE), (d) (μ-H)$MFe(CO)_6$(α-diimine(6e)) (α-diimine is either R-DAB or R-Pyca), (e) $MnFe(CO)_6$(R-N=C(H)C(H)N(H)R), (f) (μ-H)Fe-Mn(μ,μ'-N(R)CH_2CH_2N(R)).

$[CpFe(CO)_2]^-$ yielded instead of the heterodinuclear CoFe compound the dimanganese compound $Mn_2(CO)_6$(R-IAE) (Fig. 1c), which contains the 8e donating R-IAE ligand (R-IAE = 1-R-imine-2-R-amino-ethane) consisting of two R-DAB ligands that are C(imine)–C(imine) coupled [6]. Reaction, however, of $MX(CO)_3$(α-diimine) (M = Mn, Re and α-diimine = R-DAB, R-Pyca) with $[HFe(CO)_4]^-$ produced three different products: (μ-H)$MFe(CO)_6$(α-diimine(6e)) (Fig. 1d) (M = Mn, α-diimine = R-Pyca; M = Re, α-diimine = R-DAB, R-Pyca) [7], $MnFe(CO)_6$(R-N=C(H)C(H)N(H)R) (Fig. 1e), containing an azaallyl ligand, [8] and (μ-H)FeMn(μ,μ'-N(R)-CH_2CH_2N(R)) (Fig. 1f) with a diamido-ethane ligand [9]. It was therefore of interest to employ cyclopentadienyl containing compounds, since the cyclopentadienyl ring can change its mode of coordination from η^1 to η^5 depending on the electronic requirements of the metal centre.

In this paper we describe the synthesis of CpRuCl(R-DAB(4e)) (**1**) and the subsequent reaction of **1** with $[Co(CO)_4]^-$ which gives $CpRuCo(CO)_3$(R-DAB(6e)) (**2**).

Experimental

Materials and Apparatus

NMR spectra were obtained on a Bruker AC100 spectrometer. IR spectra were recorded with a Perkin-Elmer 283 spectrometer. Field desorption (FD) mass spectra were obtained with a Varian MAT 711 double focussing mass spectrometer with a combined EI/FD/FI ion source and coupled to spectro system MAT 100 data acquisition unit [10]. Elemental analyses were carried out by the section Elemental Analyses of the Institute of Applied Chemistry, TNO, Zeist, The Netherlands. Silicagel (60 Mesh) for column chromatography was activated before use. $CpRuCl(PPh_3)_2$ [11], $[Co(CO)_4]^-$, $[CpFe(CO)_2]^-$ [12], and the R-DAB ligands [13a, b] (**a**: R = i-Pr; **b**: R = t-Bu; **c**: neo-Pent; **d**: R = *p*-Tol) were prepared according to literature methods.

*Synthesis of CpRuCl(R-DAB(4e)) (**1a**: R = i-Pr; **1b**: R = t-Bu; **1c**: R = neo-Pent; **1d**: R = p-Tol)*

$CpRuCl(PPh_3)_2$ (1.4 mmol) and R-DAB (8 mmol) (**a**: R = i-Pr; **b**: R = t-Bu; **c**: neo-Pent; **d**: R = *p*-Tol) were stirred in 150 ml of refluxing toluene while a slow stream of air was passed through the solution. For R = i-Pr, R = t-Bu and R = neo-Pent a reaction time of 7 h was sufficient while for R = *p*-Tol refluxing had to be continued for 24 h for complete conversion. The colour of the solution had changed from red–orange to deep red. The solvent was evaporated, the residue was dissolved in 0.5 ml of CH_2Cl_2 and the product was separated by column chromatography. The first orange fraction (eluent hexane:diethyl ether = 4:1) contained some $CpRuCl(PPh_3)_2$ while the second red fraction contained **1** (for R = i-Pr, R = t-Bu and R = neo-Pent eluent diethyl ether; for R = *p*-Tol eluent CH_2Cl_2). The

eluent containing the product was evaporated and the complexes **1** were obtained by crystallization from hexane:diethyl ether = 1:1. Yield of **1a**, 30% (0.4 mmol); **1b**, 70% (1 mmol); **1c**, 35% (0.5 mmol); and **1d** 35% (0.5 mmol).

*Synthesis of CpRuCo(CO)$_3$(R-DAB(6e)) (**2a**: R = i-Pr and **2b**: R = t-Bu)*

A solution of 1 mmol of $[Co(CO)_4]^-$ in 20 ml of THF was added in 30 min to a stirred dark red solution of 1 mmol of **1a** or **1b** respectively in 100 ml of THF, which was at a temperature of −60 °C. After the addition was completed the solution was allowed to reach room temperature in one hour, during which time it turned red–orange. Stirring was continued for 3 h at room temperature. The solvent was evaporated and the residue was dissolved in 0.5 ml of CH_2Cl_2. The product was separated by column chromatography as a red–orange fraction (eluent hexane:diethyl ether = 4:1). The eluent containing the product was evaporated to 5 ml and the product separated as crystals upon cooling to −20 °C. Yield of both **2a** and **2b** 10% (0.1 mmol). Complexes **2a** and **2b** are thermally unstable. Even when kept at −20 °C under a nitrogen atmosphere slow decomposition occurred.

Analytical Data

FD mass spectra were recorded for all the products (see 'Supplementary Material'). The observed and calculated masses and isotopic patterns agreed well with the calculated masses and isotopic patterns. Elemental analysis for the complexes **1** gave satisfactory results (see 'Supplementary Material'). However, the thermal instability of **2a** and **2b** prohibited the measurement of satisfactory elemental analyses for these complexes.

Crystal Structure Determination of CpRuCo(CO)$_3$(t-Bu-DAB(6e)) ($RuCoC_{18}H_{25}N_2O_3$; Cyclopentadienyl-(1,4-di-tertiarybutyl-1,4-diaza-1,3-butadiene)tricarbonylrutheniumcobalt)

Crystals of the title compound are monoclinic, space group $P2_1/n$, with four molecules in a unit cell of dimensions: $a = 16.812(4)$, $b = 12.233(3)$, $c = 9.938(3)$ Å, $\beta = 105.47(3)°$, $V = 1970(2)$ Å^3 and $D_{calc} = 1.60$ g/cm^3. A total of 5920 independent reflections were measured on a Nonius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation of which 2214 reflections had intensities below the $3\sigma(I)$ level and were treated as unobserved. The structure was determined by means of the heavy atom method. A subsequent F_o synthesis revealed the remaining non-hydrogen atoms. In the F_o synthesis peaks were present indicating some disorder is occurring in the cyclopentadienyl ring and the t-butyl groups. This disorder has been neglected. Refinement proceeded by means of block-diagonal least-squares calculations, anisotropic for Ru and Co and isotropic for the remaining non-hydrogen atoms, employing unit weights. An empirical absorption correction ($\mu = 16.1$ cm^{-1} DIFABS [14a]) was applied and the anomalous scattering of Ru and Co was taken into account [14b]. The refinement converged to $R = 0.060$ and $R_w = 0.065$ for the 3706 observed reflections. The computer programs used were taken from the literature [14c]. The molecular geometry of **2b** with the numbering of the atoms is given in Fig. 2, which shows a PLUTO drawing of the molecule [14d]. Atomic parameters, bond lengths and bond angles are given in Tables I, II and III respectively. See also 'Supplementary Material'.

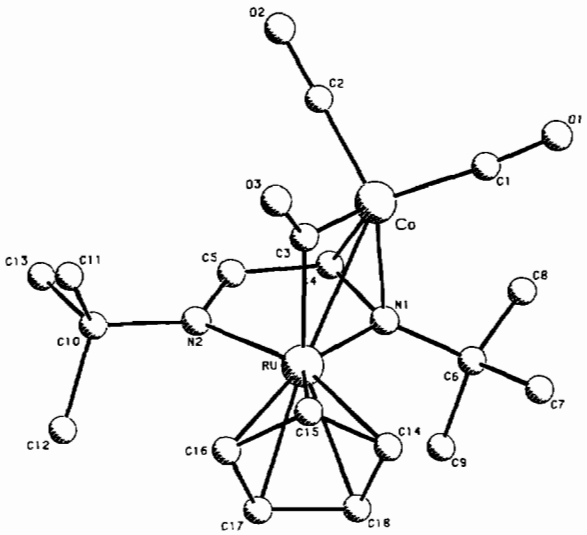


Fig. 2. Molecular geometry of CpRuCo(CO)$_3$(t-Bu-DAB(6e)) (**2b**).

Results and Discussion

Formation of Products

$CpRuCl(PPh_3)_2$ reacted with excess R-DAB in refluxing toluene to CpRuCl(R-DAB(4e)) (**1a**: R = i-Pr; **1b**: R = t-Bu; **1c**: R = neo-Pent; **1d**: R = *p*-Tol) according to eqn. (1). ^{1}H NMR and ^{13}C NMR specstroscopy indicated that in these complexes the R-DAB ligand is in a chelating 4e donating coordination mode. The reaction involves the substitution

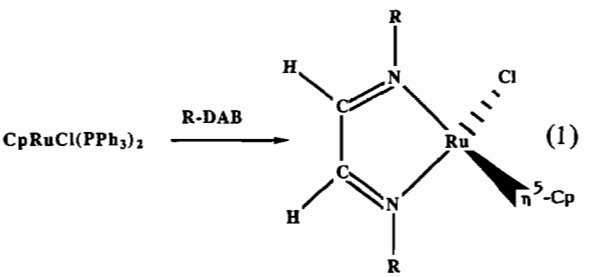


TABLE I. Fractional Coordinates of the Atoms and Equivalent Isotropic Thermal Parameters of $CpRuCo(CO)_3$(t-Bu-DAB(6e)) (**2b**)

Atom	x	y	z	U_{eq}[a]
Ru	0.13045(3)	0.22397(5)	0.44152(6)	0.0276(2)
Co	0.28326(6)	0.16182(8)	0.57147(10)	0.0324(5)
C1	0.3509(5)	0.1053(7)	0.4841(9)	0.047(2)*
C2	0.3167(5)	0.1039(7)	0.7340(8)	0.044(2)*
C3	0.1818(5)	0.0820(6)	0.5276(8)	0.039(2)*
C4	0.2708(4)	0.3218(6)	0.6350(7)	0.036(2)*
C5	0.2091(5)	0.3176(6)	0.7090(8)	0.038(2)*
C6	0.2872(5)	0.3720(7)	0.4020(8)	0.39(2)*
C7	0.2764(5)	0.3157(8)	0.2591(9)	0.051(2)*
C8	0.3797(6)	0.3877(8)	0.4717(10)	0.054(2)*
C9	0.2426(6)	0.4834(8)	0.3827(10)	0.057(2)*
C10	0.0721(5)	0.2745(7)	0.7260(8)	0.045(2)*
C11	0.0516(7)	0.1519(10)	0.7324(12)	0.073(3)*
C12	−0.0055(7)	0.3416(10)	0.6490(12)	0.079(3)*
C13	0.1040(7)	0.3185(10)	0.8759(12)	0.072(3)*
C14	0.0915(5)	0.1826(7)	0.2160(8)	0.042(2)*
C15	0.0506(6)	0.1142(8)	0.2905(10)	0.056(2)*
C16	0.0004(6)	0.1802(9)	0.3527(10)	0.061(2)*
C17	0.0117(6)	0.2929(8)	0.3181(10)	0.058(2)*
C18	0.0668(5)	0.2923(8)	0.2326(9)	0.050(2)*
N1	0.2461(3)	0.3036(4)	0.4914(6)	0.029(1)*
N2	0.1358(3)	0.2836(5)	0.6446(6)	0.035(1)*
O1	0.3973(5)	0.0613(6)	0.4345(8)	0.073(2)*
O2	0.3411(4)	0.0693(6)	0.8478(8)	0.070(2)*
O3	0.1611(4)	−0.0096(6)	0.5400(7)	0.061(2)*

[a]Starred items were refined isotropically.

TABLE II. Bond Distances (Å) of the Atoms of $CpRuCo(CO)_3$(t-Bu-DAB(6e)) (**2b**)[a]

Ru–Co	2.660(3)	C4–C5	1.423(8)
Ru–C3	2.025(6)	C4–N1	1.394(7)
Ru–C14	2.219(6)	C5–N2	1.296(8)
Ru–C15	2.187(7)	C6–C7	1.545(8)
Ru–C16	2.195(8)	C6–C8	1.537(9)
Ru–C17	2.212(7)	C6–C9	1.542(9)
Ru–C18	2.229(6)	C6–N1	1.515(7)
Ru–N1	2.113(5)	C10–C11	1.544(11)
Ru–N2	2.125(4)	C10–C12	1.558(11)
Co–C1	1.746(7)	C10–C13	1.539(10)
Co–C2	1.715(6)	C10–N2	1.509(8)
Co–C3	1.912(6)	C14–C15	1.412(9)
Co–C4	2.084(5)	C14–C18	1.427(9)
Co–N1	1.941(4)	C15–C16	1.422(10)
C1–O1	1.160(9)	C16–C17	1.446(10)
C2–O2	1.174(8)	C17–C18	1.415(10)
C3–O3	1.190(8)		

[a]e.s.d.s given in parentheses.

of the two phosphine ligands of $CpRuCl(PPh_3)_2$ by a σ,σ-N,N′ bidentate bonded R-DAB ligand.

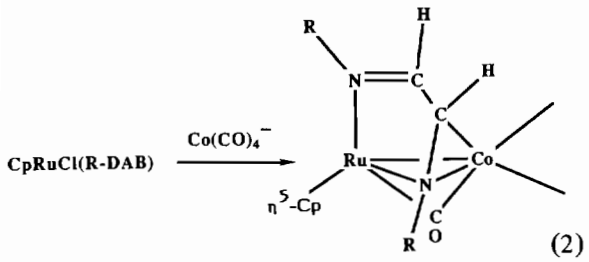
The reactions of the ruthenium halide complexes **1a** and **1b** with one equivalent of $[Co(CO)_4]^-$ affording $CpRuCo(CO)_3$(R-DAB(6e)) (**2a**: R = i-Pr and **2b**: R = t-Bu) which contain a 6e donating R-DAB ligand, are schematically depicted in eqn. (2). In the reaction of **1d** with $[Co(CO)_4]^-$ only decomposition was observed.

It is of interest to note that in the reactions of **1a** and **1b** with $[CpFe(CO)_2]^-$ only decomposition was observed and no products were isolated.

TABLE III. Bond Angles (°) of the Atoms of $CpRuCo(CO)_3$-(t-Bu-DAB(6e)) (**2b**)[a]

Co–Ru–C3	45.7(2)	C3–Co–C4	113.1(3)
Co–Ru–C14	114.3(2)	C3–Co–N1	101.1(3)
Co–Ru–C15	119.6(2)	C4–Co–N1	40.3(2)
Co–Ru–C16	148.8(2)	Co–C1–O1	174.4(5)
Co–Ru–C17	171.8(2)	Co–C2–O2	176.6(5)
Co–Ru–C18	136.1(2)	Ru–C3–Co	85.0(4)
Co–Ru–N1	46.2(2)	Ru–C3–O3	138.4(5)
Co–Ru–N2	81.1(2)	Co–C3–O3	136.5(5)
C3–Ru–C14	102.1(3)	Co–C4–C5	105.6(5)
C3–Ru–C15	83.0(4)	Co–C4–N1	64.3(4)
C3–Ru–C16	103.2(4)	C5–C4–N1	117.7(6)
C3–Ru–C17	141.4(3)	C4–C5–N2	119.0(7)
C3–Ru–C18	139.5(3)	C7–C6–C8	109.1(6)
C3–Ru–N1	92.0(3)	C7–C6–C9	110.2(6)
C3–Ru–N2	89.3(3)	C7–C6–N1	109.5(6)
C14–Ru–C15	37.4(3)	C8–C6–C9	110.2(7)
C14–Ru–C16	62.9(3)	C8–C6–N1	111.7(6)
C14–Ru–C17	63.1(3)	C9–C6–N1	106.1(6)
C14–Ru–C18	37.4(3)	C11–C10–C12	111.4(8)
C14–Ru–N1	110.3(3)	C11–C10–C13	108.9(8)
C14–Ru–N2	164.5(2)	C11–C10–N2	106.9(7)
C15–Ru–C16	37.9(3)	C12–C10–C13	108.8(8)
C15–Ru–C17	63.6(4)	C12–C10–N2	108.6(8)
C15–Ru–C18	62.4(3)	C13–C10–N2	112.3(7)
C15–Ru–N1	143.4(3)	Ru–C14–C15	70.1(5)
C15–Ru–N2	136.5(3)	Ru–C14–C18	71.7(5)
C16–Ru–C17	38.3(3)	C15–C14–C18	107.4(8)
C16–Ru–C18	62.5(3)	Ru–C15–C14	72.6(6)
C16–Ru–N1	164.3(3)	Ru–C15–C16	71.4(6)
C16–Ru–N2	104.6(3)	C14–C15–C16	108.7(8)
C17–Ru–C18	37.1(3)	Ru–C16–C15	70.8(6)
C17–Ru–N1	126.3(3)	Ru–C16–C17	71.5(6)
C17–Ru–N2	101.5(3)	C15–C16–C17	107.9(9)
C18–Ru–N1	103.2(3)	Ru–C17–C16	70.2(6)
C18–Ru–N2	130.1(3)	Ru–C17–C18	72.1(6)
N1–Ru–N2	79.4(3)	C16–C17–C18	106.6(8)
Ru–Co–C1	123.0(3)	Ru–C18–C14	70.9(5)
Ru–Co–C2	127.4(3)	Ru–C18–C17	70.8(6)
Ru–Co–C3	49.3(2)	C14–C18–C17	109.4(7)
Ru–Co–C4	73.5(2)	Ru–N1–Co	81.9(3)
Ru–Co–N1	51.8(2)	Ru–N1–C4	108.5(4)
C1–Co–C2	102.2(4)	Ru–N1–C6	130.7(4)
C1–Co–C3	110.1(4)	Co–N1–C4	75.4(4)
C1–Co–C4	130.8(3)	Co–N1–C6	125.9(4)
C1–Co–N1	109.3(4)	C4–N1–C6	117.1(5)
C2–Co–C3	93.0(4)	Ru–N2–C5	111.9(5)
C2–Co–C4	97.9(4)	Ru–N2–C10	128.9(4)
C2–Co–N1	138.1(3)	C5–N2–C10	118.4(7)

[a]e.s.d.s given in parentheses.



(2)

Before discussing the possible reaction routes in more detail the identification of the products by ^1H NMR, ^{13}C NMR, and IR spectroscopy and the molecular structure of **2b** will be discussed.

Molecular Geometry of $CpRuCo(CO)_3$(t-Bu-DAB(6e)) (2b)

The molecular geometry of **2b** together with the atomic numbering is given in Fig. 2. The bond lengths and angles are given in Tables II and III.

As shown in the Figure the molecule comprises a Ru–Co bond with a length of 2.660(3) Å. This value lies in between the value for the Ru–Ru single bond length of 2.854(3) Å in $Ru_3(CO)_{12}$ [15] and the Co–Co single bond length of 2.522(2) Å in $Co_2(CO)_8$ [16] and is for example similar to that of 2.648(1) Å in $RuCo(CO)_6(Ph_2PC(O)C(Ph)C(Ph))$ [17]. The cyclopentadienyl group is η^5-coordinated to ruthenium with an average Ru–C distance of 2.208(3) Å. The metal carbonyl part of the molecule consists of two terminal carbonyl ligands bonded to cobalt [Co–C(1) = 1.746(7), Co–C(2) = 1.715(6) Å] and a third carbonyl ligand that is slightly asymmetrically bridging the Ru–Co bond with Ru–C(3) = 2.025(6) and Co–C(3) = 1.912(6) Å. That the latter bond length is shorter can be attributed to the shorter covalent radius of cobalt with respect to ruthenium. The Ru–C(3)–O(3) and Co–C(3)–O(3) bond angles are 138.4(5)° and 136.5(5)° respectively. The 6e donor R-DAB ligand is coordinated to Ru via N(1) and N(2) with approximately equal bond lengths: Ru–N(1) = 2.113(5) and Ru–N(2) = 2.125(4) Å. The values are similar to those of 2.15(1) Å found in $Ru_2(CO)_4$(i-Pr-DAB(6e))$_2$, containing two 6e donating i-Pr-DAB ligands [18]. The C(4)N(1) part of the ligand is η^2-coordinated to cobalt with slightly different bond lengths: Co–C(4) = 2.084(5) and Co–N(1) = 1.941(4) Å. N(1) is slightly asymmetrically bridging the Ru–Co bond with the Co–N(1) being shorter than the Ru–N(1), similar to the Co–C(3) and Ru–C(3) of the bridging carbonyl group. These structural features may be compared to those of $MnCo(CO)_6$(i-Pr-DAB(6e)) [14] for which a structure determination revealed that it contained a 6e donating i-Pr-DAB ligand, with one imine bond being coordinated to cobalt, and a semibridging carbonyl group. For the η^2-coordinated part of the ligand in $MnCo(CO)_6$(i-Pr-DAB(6e)) Co–C and Co–N distances of 2.065(11) and 1.891(9) Å, respectively, were observed.

The imine C(5)=N(2) bond length of the σ-coordinated part of the ligand is 1.296(8) Å. This bond is only slightly elongated as compared to the $C(sp_2)$=$N(sp^2)$ double bond of 1.258(3) in free c-Hex-DAB [19]. However, the η^2-coordinated imine bond C(4)–N(1) is elongated to 1.394(7) Å, which is close to the value of 1.358(4) Å found for the η^2-C=N bonded imine moiety in $MnCo(CO)_6$(i-Pr-DAB(6e)). This extensive bond lengthening upon η^2-C=N coordination is explained by π-backbonding from Co into the π^*-orbital of the C=N unit which is antibonding between C and N [2a]. The central C(4)–C(5) distance of 1.423(8) Å is normal for a single $C(sp^2)$–$C(sp^2)$ bond and similar to that of 1.457(3) Å found in free c-Hex-DAB.

IR, ^1H and ^{13}C NMR Spectroscopy

Complexes 1

The ^1H and ^{13}C NMR data of the CpRuCl(R-DAB(4e)) (**1**) complexes are listed in Table IV and V, respectively.

The chemical shifts of the imine protons and carbon atoms are indicative of the coordination mode of the ligand and may give information about the electronic distribution in the imine skeleton [2a–c]. In the ^1H NMR spectra of the complexes **1** the resonances of the imine protons are found around 8.3 ppm which is indicative of for a σ,σ-N,N coordination mode of the ligand. This value may be compared with the 8 ppm value for these protons in the free ligand [2a] and with that of 8.2 ppm for those in the Ru(II) complex $[RuCl(\eta^6\text{-}C_6H_6)$(R-DAB(4e))]$BF_4$ [20] but they are downfield to the value of 7.10 ppm for the imine protons in the Ru(0) complex $Ru(CO)_3$(diisopropylmethyl-DAB(4e)) [21]. Similar comparisons may be made for the resonances of the imine carbon atoms of the complexes **1** that are found around 155 ppm. This value may be compared with the 158 ppm value for the free ligand and (since no data for ruthernium complexes with chelating R-DAB ligands are available) the 159 ppm value for $MnBr(CO)_3$(R-DAB(4e)) [22] but differs significantly from the 143 ppm value for the imine carbon resonances in $Fe(CO)_3$(R-DAB(4e)) [23].

The zerovalent complexes show an upfield shift for the imine protons and carbon atoms compared to the free ligand values which can be explained by backdonation from the metal into the π^*-orbital of the imine unit. However, for the $CpRu^{II}Cl$(R-DAB(4e)) complexes, for $[Ru^{II}Cl(\eta^6\text{-}C_6H_6)$(R-DAB(4e))]$BF_4$ and also for $Mn^{I}Br(CO)_3$(R-DAB(4e)) the chemical shifts of the imine protons and carbon atoms do not indicate an important delocalization of the positive charge through the metalladiazacyclic ring.

TABLE IV. ^{1}H NMR Data of CpRuCl(R-DAB(4e)) (**1a**: R = i-Pr; **1b**: R = t-Bu; **1c**: R = neo-Pent and **1d**: R = *p*-Tol)[a]

R group		Cp	Imine H
1a	1.50(d, 6 Hz, 6H)/1.52(d, 6 Hz, 6H); 4.60(sept, 6 Hz, 2H)	4.53(s, 5H)	8.36(s, 2H)
1b	1.65(s, 18H)	4.55(s, 5H)	8.49(s, 2H)
1c	1.11(s, 18H); 4.12(s, 4H)	4.50(s, 5H)	8.15(s, 2H)
1d	2.39(s, 6H); 7.18(d, 8 Hz, 4H); 7.69(d, 8 Hz, 4H)	4.39(s, 5H)	8.49(s, 2H)

[a]The values (ppm relative to TMS) have been obtained in chloroform-d_1 solutions at 100 MHz. Vettical bars separate diastereotopic pairs; s = singlet, d = doublet, sept = septet.

TABLE V. ^{13}C NMR Data of CpRuCl(R-DAB(4e)) (**1a**: R = i-Pr; **1b**: R = t-Bu; **1c**: R = neo-Pent and **1d**: R = *p*-Tol)[a]

	R group	Cp	Imine C
1a	23.5/23.9; 66.0	75.6	154.5
1b	32.0; 66.2	71.4	156.7
1c	29.2; 34.1; 78.9	77.8	160.4
1d	21.3; 122.0; 129.6; 138.0; 153.6	80.0	156.5

[a]The values (ppm relative to TMS) have been obtained in chloroform-d_1 solutions on a Bruker AC100 using an attached proton test pulse sequence.

The R groups of both ligand halves of the R-DAB ligands in the complexes **1** are equivalent, which is implied by the observation of a single set of resonances for these R groups in the ^{1}H NMR and ^{13}C NMR spectra. In the ^{1}H NMR spectrum of **1a** two doublets are observed for the isopropyl methyl groups. The non-equivalence of the two methyl groups is also obvious from the two distinct resonances at 23.5 and 23.9 ppm for the methyl groups in the ^{13}C NMR spectrum. This is in accord with the diastereotopic nature of the methyl groups in the isopropyl substituents. In the ^{1}H NMR spectrum of **1c** only a singlet for the CH_2-protons of both neopentyl groups is observed, whereas an AB pattern was expected. This may be explained by a too small chemical shift difference for these CH_2-protons. Another explanation could be that a fluxional process is taking place that renders these protons isochronous which process, however, must be very rapid because even at 183 K no broadening of the ^{1}H NMR sigals was observed. Therefore the occurrence of such a fluxional process seems unlikely since no such processes are observed for similar compounds containing for example chelating phosphine ligands [24].

In the ^{1}H and ^{13}C NMR spectra the cyclopentadienyl protons and carbon atoms give rise to resonances at 4.5 and 75 ppm, respectively. These values are comparable to those found for many other cyclopentadienyl–Ru^{II} complexes [24, 25].

Complexes 2

The ^{1}H NMR data of the $CpRuCo(CO)_3$(R-DAB(6e)) complexes (**2a** and **2b**) are listed in Table VI together with the IR data in the ν(CO) region. The latter show the presence of two absorptions in the terminal ν(CO) region and one absorption around 1812 cm^{-1} which is in accord with the presence of a bridging carbonyl ligand as was also apparent from the single crystal X-ray structure determination for **2b** (*vide supra*).

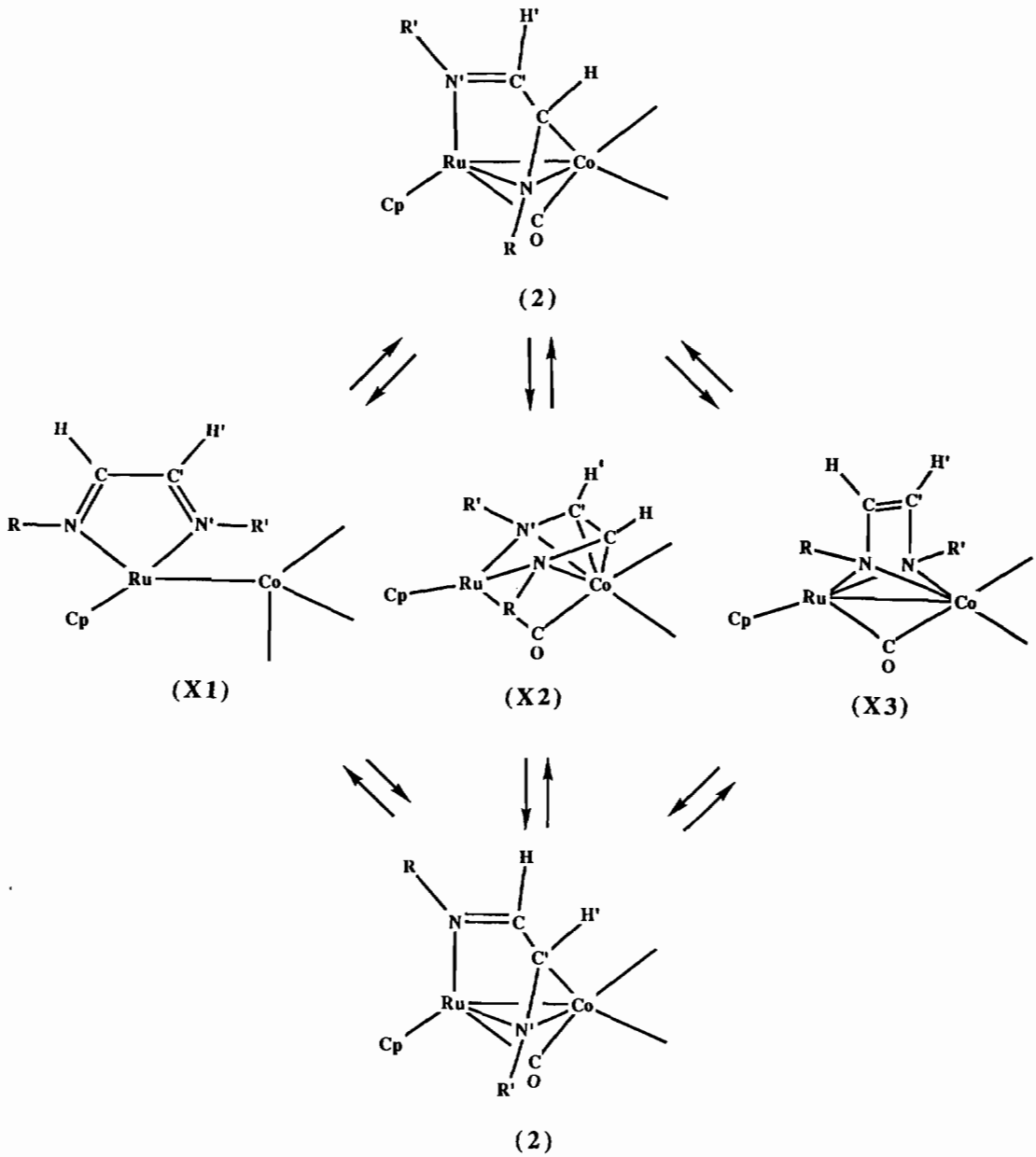
In the ^{1}H NMR spectra of **2a** and **2b** the resonances of the cyclopentadienyl protons were observed around 4.95 ppm.

The 6e coordination mode for the R-DAB ligand is in general obvious from the ^{1}H NMR data. When a R-DAB ligand is in the 6e coordination mode separate sets of signals are observed for the two R groups and the resonance of the imine proton attached to the η^2-C=N coordinated part of the

TABLE VI. IR and ^{1}H NMR Data of $CpRuCo(CO)_3$(R-DAB(6e)) (**2a**: R = i-Pr and **2b**: R = t-Bu)

	IR (ν(CO) in hexane)	Chemical shifts[a]		
		R group	Cp	Imine H
2a	2007, 1948, 1814	1.02(d, 6 Hz, 3H)/1.06(d, 6 Hz, 3H) 1.42(d, 6 Hz, 3H)/1.48(d, 6 Hz, 3H) 3.56(sept, 6 Hz, 1H); 3.90(sept, 6 Hz, 1H)	4.92(s, 5H)	5.25(s, 1H); 7.67(s, 1H)
2b	2000, 1947, 1810	1.16(s, 9H); 1.41(s, 9H)	4.97(s, 5H)	5.24(s, 1H); 7.72(s, 1H)

[a]The values (ppm relative to TMS) have been obtained at 225 K in acetone-d_6 solutions at 100 MHz. Vertical bars separate diastereotopic pairs; s = singlet, d = doublet, sept = septet.



Scheme 1. Proposed mechanisms for the exchange process as observed in the ^1H NMR spectra of $CpRuCo(CO)_3$(R-DAB(6e)) (**2a** and **2b**).

ligand is drastically shifted upfield. Interestingly in the room temperature ^1H NMR spectra of **2a** and **2b** only a single set of lines is found for both R groups and no clear resonance for the imine protons was observed. Obviously there is a fluxional process taking place that involves the interchange between the η^2-C=N coordinated and the σ-N coordinated part of the R-DAB ligand. This was confirmed by variable temperature NMR experiments in the temperature range of 253 to 360 K. For **2b** at 253 K in acetone-d_6 two separate lines for the two t-Bu-groups and two resonances at 7.70 and 5.28 ppm for the imine protons attached to respectively the σ-N and η^2-C=N coordinated parts of the ligand were observed. The resonances of respectively the t-Bu groups and imine protons coalesced at about 262 and 285 K to resonances at 1.30 and 6.49 ppm. A ΔG of 55 kJ/mol was calculated. At 360 K in toluene-d_8 single coalesced resonances were found respectively at 1.34 and 5.90 ppm for the t-Bu-groups and the imine protons. The coalesced signal at 5.90 ppm in toluene-d_8, when compared with the signal at 6.49 ppm in acetone-d_6, indicates a very strong solvent dependence of the chemical shifts

of the imine protons. The slow exchange limits of the t-Bu and imine proton signals in toluene-d_8 could unfortunately not be measured owing to viscosity problems.

For **2a** in acetone-d_6 a similar behaviour was observed with coalescence temperatures of 275 and 287 K for the i-Pr groups and imine protons respectively (Table VI) and a ΔG of 56 kJ/mol was calculated.

Three possible intermediates (and mechanisms) may be put forward to explain this exchange process (see Scheme 1). The first intermediate involves the dissociation of the η^2-C=N bond, forming an intermediate with a vacant coordination site on Co and with the R-DAB ligand σ,σ-N,N′ coordinated to Ru (**X1**). In the second intermediate the Ru–Co bond is broken and the second imine bond η^2-coordinated, creating an 8e coordinated R-DAB ligand (**X2**). The third intermediate involves the dissociation of the η^2-C=N bond together with the movement of the R-DAB ligand to a symmetrically bridging coordination mode (**X3**). From all three intermediates the initial situation can be restored by the reverse reaction with either one of the C=N bonds. The first two intermediates are proposed for the fluxional behaviour of the 6e coordinated R-DAB ligand in $MnCo(CO)_6$(c-Pr-DAB; Me, Me(6e)), in which methyl groups are attached to the imine carbon atoms instead of hydrogen atoms [4]. The third intermediate has been proposed by Frühauf *et al.* to explain the photochemical interconversion of the σ-N and η^2-C=N moieties of the R-DAB ligand in $Fe_2(CO)_5(P(OMe)_3)$(R-DAB(6e)) [26]. Interestingly $MnCo(CO)_6$(c-Pr-DAB; Me, Me(6e)) is the only other example of a complex with a fluxional 6e coordinated R-DAB ligand. However, for this type of ligand the fluxionality may be rationalized by the observation that C(Me)=N bonds are weaker π-acceptors than C(H)=N bonds [2a]. Consequently $MnCo(CO)_6$(R-DAB(6e)) showed no fluxional behaviour. Apparently this subject needs further investigation for a proper rationalization of these observations.

Reaction Routes

The reaction of $CpRuCl(PPh_3)_2$ with R-DAB giving the CpRuCl(R-DAB(4e)) (**1**) complexes may be viewed as a simple substitution of the phosphine ligands by a chelating R-DAB ligand. Substitution reactions with $CpRuCl(PPh_3)_2$ are well documented and are observed to proceed more readily than those with $CpRuCl(CO)_2$ of which the carbonyl ligands are difficult to replace. For example the reaction of $CpRuCl(PPh_3)_2$ with a whole range of diphosphine ligands afforded CpRuCl(diphosphine) [24, 25]. Simple substitution reactions involving R-DAB and giving complexes with chelating R-DAB ligands are well known, e.g. reactions of R-DAB with $[RuCl(\eta^6\text{-}C_6H_6)(MeCN)_2]^+$, $MnBr(CO)_5$, $Mo(CO)_6$ and $Co(\eta^5\text{-}C_5H_5)(CO)_2$ afforded $[RuCl(\eta^6\text{-}C_6H_6)$(R-DAB(4e))$]^+$ [20], $MnBr(CO)_3$(R-DAB(4e)) [22], $Mo(CO)_4$(R-DAB(4e)) [27] and $Co(\eta^5\text{-}C_5H_5)$-(R-DAB(4e)) [28] respectively.

The reaction of **1** with $[Co(CO)_4]^-$ gave the expected complexes $CpRuCo(CO)_3$(R-DAB(6e)) (**2**). Five possible reaction routes for the interaction of metal carbonyl anions with complex metal halides have been suggested [29a–d]. However, in the reaction between **1a** or **1b** with $[Co(CO)_4]^-$ only heterodinuclear products **2** are obtained. Therefore, a substitution reaction, in which Cl^- is replaced by $[Co(CO)_4]^-$, is strongly indicated to be the first step in the reaction sequence. During this step the Ru–Co bond is formed while the R-DAB ligand remains σ,σ-N,N′ coordinated to ruthenium only. The next step is most likely an associative substitution process or a concerted nucleophilic substitution process in which a carbonyl group on cobalt is replaced by an imine group that becomes η^2-coordinated to cobalt. Alternatively, a carbonyl may be eliminated from cobalt first, thereby creating a vacant coordination site which is filled by an imine group that becomes η^2-coordinated.

The reaction of **1** with $[Co(CO)_4]^-$ to give the complexes **2** is comparable with the reaction of $MnBr(CO)_3$(R-DAB(4e)) with $[Co(CO)_4]^-$ which afforded $MnCo(CO)_6$(R-DAB(6e)). When using a stronger nucleophile e.g. $[CpFe(CO)_2]^-$ the reactions are less straightforward. In the reaction of **1** with $[CpFe(CO)_2]^-$ only decomposition was observed whereas the reaction of $MnBr(CO)_3$(R-DAB(4e)) with $[CpFe(CO)_2]^-$ gave $Mn_2(CO)_6$(R-IAE) [6]. The latter behaviour might be explained by the observation that, as compared with the weaker metal carbonyl nucleophiles, the stronger are less well suited for the synthesis of heteronuclear compounds in reactions of metal carbonyl anions with metal halides [30a–c, 31].

Supplementary Material

Listings of FD mass data, elemental analysis data, anisotropic thermal parameters, observed and calculated structure factors are available from the authors on request.

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