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Contribution from the Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, J. H. van't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, FB 6-Fachgebiet Organische Chemie der Universität-GH-Duisburg, Lotharstrasse 1, D-4100 Duisburg 1, Bundesrepublik Deutschland, and Laboratorium voor Kristallografie, Universiteit van Amsterdam, J. H. van't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Facile Preparation of $Ru(CO)_3$(R-DAB) and Its Relation to the Reversible C–C Bond Formation and Fission between Two R-DAB Ligands on a Diruthenium Fragment[1]

Wilhelmus P. Mul,[†] Cornelis J. Elsevier,*[,†] Hans-Werner Frühauf,[†] Kees Vrieze,[†] Ingrid Pein,[‡]
Martin C. Zoutberg,[§] and Casper H. Stam[§]

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$Ru(CO)_5$ reacts with 1,4-diaza-1,3-butadienes (R-DAB; R = *i*-Pr (**a**), c-Hex (**b**), *t*-Bu (**c**), *p*-Tol (**d**)) to yield $Ru(CO)_3$(R-DAB) (**6a–d**) together with a small amount of $Ru_2(CO)_6$(R-DAB) (**1a–c**) and an unidentified, probably organic product. The known complexes $Ru_2(CO)_5$(R-ADA) (**7a,b**; R-ADA = 1,6-di-R-1,6-diazahexa-1,5-diene-3,4-di-R-aminato), containing two C–C-coupled R-DAB ligands, and $Ru_2(CO)_4$(*p*-Tol-DAB)$_2$ (**8d**), containing two σ-N,σ-N′,η^2-C=N′-coordinated R-DAB ligands, react with CO at elevated temperatures to yield $Ru(CO)_3$(R-DAB) (**6a,b,d**) as pure compounds in solution. The extremely air-sensitive mononuclear products (**6**) have been characterized by IR, ^{1}H NMR, ^{13}C NMR, and FD mass spectroscopy. The reactions are reversible. Photochemical or thermal activation of **6a,b,d** in solution results in the re-formation of **7a,b** or **8d**, respectively. Irradiating a solution of **6a** at −70 °C yields a dark purple compound (I), which, on the basis of its chemical reactivity, is proposed to be an intermediate in the reversible C–C coupling/fission processes between two R-DAB ligands (**7a,b** $\rightleftharpoons$ **6a,b**). Irradiating a solution of **6d** in the presence of free *p*-Tol-DAB gives rise to another reaction that involves the formation of Ru(*p*-Tol-DAB)$_2$(CO)$_2$ (**10d**) and Ru(*p*-Tol-DAB)$_3$ (**11d**). The C–C-coupled compound $Ru_2(CO)_5$(*i*-Pr-ADA) (**7a**) has been characterized by an X-ray structure determination. Crystals of **7a**, $C_{21}H_{32}N_4O_5Ru_2$, are monoclinic, space group $P2_1/a$, with cell constants a = 20.735 (6) Å, b = 15.847 (4) Å, c = 8.034 (2) Å, β = 100.25 (3)°, and Z = 4. A total of 2117 absorption corrected reflections have been used in the refinement resulting in a final R value of 0.054. The molecule consists of two $Ru(CO)_2$ units bridged by a CO ligand and a formally 10e-donating *i*-Pr-ADA ligand. The observed short internuclear distance of 2.873 (2) Å is assumed to be a result of the bridging ligands forcing the metal atoms into proximity, since, on the basis of CVMO theory, no metal–metal bond is expected to be present. Furthermore, detailed information about the interconversions between R-DAB and R-ADA complexes has been acquired. It has been found, for instance, that the isomerization of $Ru_2(CO)_4$(R-ADA) (**9a,b**) to $Ru_2(CO)_4$(R-DAB)$_2$ (**8a,b**) only proceeds in the presence of a catalytic amount of CO. The corresponding catalytic cycle is discussed.

Introduction

Reactions of 1,4-diaza-1,3-butadienes (R-DAB)[2] with metal carbonyls of the iron triad lead to the formation of several mono-, di-, and polynuclear complexes.[3] The availability of both the lone pairs on the N atoms and the imine π-bonds for coordination results in a flexible coordination behavior in which the R-DAB ligand can donate up to 8 electrons to the metal centers.

An interesting aspect of the coordinated R-DAB ligand is the possibility of activation of the imine C atom toward C–C coupling reactions. Reactions involving C–C bond formation (and fission) in the coordination sphere of metal center(s) are of particular interest with respect to carbon chain growth and metathesis on metal surfaces in heterogeneous catalysis.[4] This subject has resulted in the development of a rich chemistry and continues to attract attention. For instance, the dinuclear complex $Ru_2(CO)_6$(R-DAB) (**1**), containing a bridging 6e σ-N,μ_2-N′,η^2-C=N′-coordinated R-DAB ligand has been shown to give C–C coupling products in reactions with unsaturated substrates such as electron-deficient alkynes (**2**; Figure 1),[5] diimides,[6] sulfines,[6] and R-DAB.[7] The corresponding dinuclear iron analogues are not involved in C–C coupling reactions between the coordinated R-DAB ligand and alkynes but favor N–C coupling reactions, reflecting the decisive influence of the metal involved.[8]

Selective C–C coupling of organic fragments has also been observed for mononuclear $Fe(CO)_3$(R-DAB) (**3**) complexes, containing a chelating 4e σ-N,σ-N′-coordinated R-DAB ligand.[9] In the presence of an additional ligand such as CO or PR_3, these complexes react with electron-deficient alkynes to give finally the 1,5-dihydropyrrol-2-one-containing compound **5**. In this reaction, in which a CO ligand, an alkyne, and an R-DAB ligand are selectively coupled, the intermediacy of **4** was observed (Figure 2).

One of our objectives has been to extend this chemistry by studying also reactions of mononuclear $Ru(CO)_3$(R-DAB) (**6**) with acetylenes, in order to obtain an extension of our understanding of factors affecting C–C and C–N coupling with R-DAB. Except for R-DAB ligands containing bulky substituents (R = 2,4,6-mesityl, 2,6-xylyl, (*i*-Pr)$_2$CH),[10] however, no straightforward

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[†] Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam.
[‡] Universität Duisburg.
[§] Laboratorium voor Kristallografie, Universiteit van Amsterdam.

(1) Ruthenium Carbonyl 1,4-Diaza-1,3-butadienes (R-DAB) Complexes. 10. For earlier parts see refs 5, 6, 7, 10, and 19.

(2) The relevant abbreviations used throughout this text are as follows. The 1,4-diaza-1,3-dienes of formula RN=C(H)C(H)=NR are abbreviated as R-DAB. R-ADA stands for 1,6-di-R-1,6-diazahexa-1,5-diene-3,4-di-R-aminato, RN=C(H)(H)C(NR)(H)C(NR)C(H)=NR, the reductively C–C-coupled formally dianionic dimer of R-DAB ligated to two metal atoms. We note that we have, as suggested by one of the reviewers, changed the formerly applied nomenclature for this C–C-coupled ligand, from IAE to ADA. The pyridinecarbaldehyde imines of formula 6-R′C_5H_3N-2-(C(H)=NR) are abbreviated as R-Pyca. The 1,2-di-R-aminato-1,2-bis(2-pyridyl)ethane, [6-R′C_5H_3N-2]CH(NR)CH(NR)[2-C_5H_3N-6-R′], the C–C-coupled dimer of R-Pyca, will be abbreviated to R-APE.

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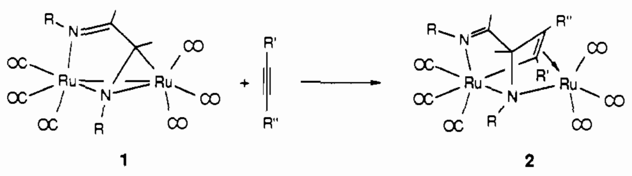

Figure 1. Reaction of 6e-coordinated R-DAB (R = *t*-Bu) with electron-deficient alkynes (R' = R'' = CF$_3$; R' = R'' = C(O)OMe; R' = C(O)OMe, R'' = H; R' = Ph, R'' = H) on a dinuclear ruthenium unit.

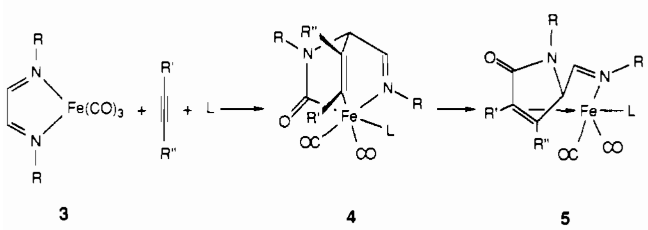

Figure 2. Reaction of 4e-coordinated R-DAB with an electron-deficient alkyne on a mononuclear iron unit.

synthesis for mononuclear Ru(CO)$_3$(R-DAB) (**6**) was available. In this paper we will present the results of an investigation aiming at the preparation of Ru(CO)$_3$(R-DAB) (R = *i*-Pr (**6a**), c-Hex (**6b**), *t*-Bu (**6c**), *p*-Tol (**6d**)). Also the reversible C–C coupling of two R-DAB ligands on ruthenium carbonyl centers has been (re)investigated in detail. Furthermore, the X-ray crystal structure of the C–C-coupled product, Ru$_2$(CO)$_5$(*i*-Pr-ADA)[2] (**7a**), which is also an important precursor of Ru(CO)$_3$(*i*-Pr-DAB) (**6a**), is described.

Experimental Section

Materials and Apparatus. ^{1}H and ^{13}C NMR spectra were obtained on Bruker AC100 and WM250 spectrometers. IR spectra were recorded with Perkin-Elmer 283 and Nicolet 7199 B FT-IR spectrophotometers using matched NaCl solution cells of 0.5-mm path length. Field desorption (FD) mass spectra[11] were obtained with a Varian MAT-711 double-focusing mass spectrometer with a combined EI/FI/FD source, fitted with a 10-μm tungsten wire FD emitter containing carbon microneedles with an average length of 30 μm, using emitter currents of 0–15 mA. The ion source temperature was generally 50–120 °C. Elemental analysis were carried out by the Elemental Analysis section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

Solvents were carefully dried and distilled prior to use. All preparations were carried out under an atmosphere of dry nitrogen by using Schlenk techniques. Silica gel for column chromatography (kieselgel 60, 70–230 mesh, E. Merck, Darmstadt, West Germany) was dried before use. Ru$_3$(CO)$_{12}$ was used as purchased from Strem Chemicals, Inc. Ru(CO)$_5$ was photochemically prepared from Ru$_3$(CO)$_{12}$ by published procedures;[12] the yields, however, were far from quantitative due to the formation of a highly insoluble red/purple product for which a polymeric structure, [Ru(CO)$_4$]$_n$, was proposed by Baird et al.[13] For the photolysis experiments an Oriel mercury-arc source equipped with an Osram 200-W mercury lamp was used. Ru$_2$(CO)$_6$(*t*-Bu-DAB) (**1c**), Ru$_2$(CO)$_5$(R-ADA) (R = *i*-Pr (**7a**), c-Hex (**7b**), *t*-Bu (**7c**)), Ru$_2$(CO)$_4$(R-DAB)$_2$ (R = *i*-Pr (**8a**), *p*-Tol (**8b**)), and Ru$_2$(CO)$_4$(R-ADA) (R = *i*-Pr (**9a**), c-Hex (**9b**)) were synthesized as published before.[7a] R-DAB (R = *i*-Pr (**a**) c-Hex (**b**), *t*-Bu (**c**), *p*-Tol (**d**)) ligands were prepared according to standard procedures.[14]

Synthesis of Ru(CO)$_3$(R-DAB) (6). Method i. Under the exclusion of light Ru(CO)$_5$ (ca. 0.2 mmol) and R-DAB (**a–d**; ca. 4 mmol) were stirred at room temperature in 150 mL of hexane for about 8 h. During this time the color of the solution changed from colorless (**a–c**) or slightly yellow (**d**) to blood red (**a,b,d**) or purple (**c**). IR spectroscopy (hexane solution) in the ν(CO) region (1600–2200 cm^{-1}) showed the presence of **6a–d** together with small amounts of Ru$_2$(CO)$_6$(R-DAB) (**1a–c**) and an absorption band at 1752 cm^{-1} of unknown origin. The relative amount of **1** depended on the R group of the DAB ligand: **1a,b**, ca. 5%; **1c**, ca. 20%; **1d**, 0%. The excess of R-DAB used could be removed by washing the hexane solution twice with 50 mL of carefully deoxygenated 0.1 M HCl in water followed by washing with a concentrated NaHCO$_3$ solution and subsequently drying the solvent on Na$_2$SO$_4$.

Method ii. A solution (or suspension) of Ru$_2$(CO)$_5$(R-ADA) (**7a,b**; 0.2 mmol) in heptane or toluene (100 mL) was stirred under an atmosphere of CO for 15 min at 90 °C. The color of the solution turned from orange to intensive red. IR spectroscopy showed the presence of almost pure **6a** or **6b**, respectively. When Ru$_2$(CO)$_5$(*p*-Tol-ADA) (**7d**) was used as the starting material, complete conversion into **6d** was observed within a few minutes at room temperature.

Method iii. A solution (or suspension) of Ru$_2$(CO)$_4$(*p*-Tol-DAB)$_2$ (**8d**; 0.2 mmol) in hexane or toluene (100 mL) was stirred under an atmosphere of CO at room temperature (or 60 °C) for about 2 days (10 min). The color of the solution turned from yellow to red. IR spectroscopy revealed the presence of three intense bands in the ν(CO) region, which could be ascribed to **6d**.

Reactions of Ru(CO)$_3$(R-DAB) (6). Thermolysis. A solution of **6a–d** prepared in situ as described above was heated at reflux for about 2 h under an atmosphere of nitrogen. After this period the intensive red or purple solution had become orange (**a–c**) or yellow (**d**). Cooling the reaction mixtures at −80 °C resulted in the precipitation of **7a–c** or **8d**, respectively, in nearly quantitative yields, as indicated by spectroscopic measurements (IR, ^{1}H NMR, FD mass spectroscopy).

Photolysis. A heptane or toluene solution containing **6a–d** was irradiated by using a glass-filtered high-pressure Hg lamp. After a period of ca. 15 min, the formerly intense color had disappeared and an orange precipitate of **7a–c** or a yellow precipitate of **8d** was formed. In the presence of *p*-Tol-DAB, **6d** decomposed photochemically with formation of a dark green solution that showed two intense IR absorptions in the ν(CO) region. The extremely air-sensitive compounds present in this solution have been identified as Ru(CO)$_2$(*p*-Tol-DAB)$_2$ (**10d**) and Ru(*p*-Tol-DAB)$_3$ (**11d**) by FD mass spectroscopy (Table II). When the sun was used as the sole light source, only **10d** (IR, FD mass spectroscopy) was formed.

Removal of the Solvent. The solvent (heptane or toluene) was removed from a solution of **6a** or **6d** at reduced pressure. During this period an yellow/orange precipitate (**7a** or **7d**) was formed. After complete removal a brown/black (**a**) or brown (**d**) residue remained. After a few days both residues had become brown and were analyzed as **7a** and **7d** (impure), respectively (IR, FD mass spectroscopy). All attempts to isolate the new compound **7d** as a pure solid sample failed due to partial break up to **8d** during crystallization efforts. ^{1}H NMR of **7d** (δ in ppm relative to MeSi$_4$, CD$_2$Cl$_2$, 293 K, 100 MHz): 2.24, 2.32 (6 H, 6 H, s, s, CH$_3$); 4.47 (2 H, br s, N-CH); 6.91–7.23 (8 H, 8 H, m, m, aryl); 8.78 (2 H, br s, N=CH).

Reactions of Ru$_2$(CO)$_5$(R-ADA) (7). Thermolysis. Refluxing a toluene solution (30 mL) of **7a,b** (0.5 mmol) during 16 h yielded Ru$_2$(CO)$_4$(R-ADA) (**9a,b**), contaminated with ca. 10% of Ru$_2$(CO)$_4$(R-DAB)$_2$ (**8a,b**). After workup,[7a] **9a,b** were isolated in a yield of about 85%. When the reaction was carried out in refluxing xylene, the only product observed after 16 h was Ru$_2$(CO)$_4$(R-DAB)$_2$ (**8a,b**; yield after workup ca. 90%). The products were identified by IR, ^{1}H NMR, and FD mass spectroscopy.

Photolysis. A THF solution (30 mL) of **7a–c** (0.2 mmol) was irradiated at room temperature by a 200-W high-pressure Hg lamp until the ν(CO) pattern of **7a–c** was replaced (2–5 h) by that of **9a–c**, respectively. The yields of **9a–c** after workup as published before[7a] were almost quantitative (90%). The new compound **9c** was characterized by IR, ^{1}H NMR, and FD mass spectroscopy, and a microanalysis was carried out. Anal. Found (calcd) for C$_{24}$H$_{40}$N$_4$O$_4$Ru$_2$ (**9c**): C, 43.66 (44.30); H, 6.24 (6.20); N, 8.39 (8.61). ^{1}H NMR of **9c** (δ in ppm relative to Me$_4$Si, CDCl$_3$, 293 K, 100 MHz): 1.19, 1.36 (18 H, 18 H, s, s, *t*-Bu); 3.72 (2 H, d, J = 2 Hz, N—CH); 8.18 (2 H, d, J = 2 Hz, N=CH).

Synthesis of Ru$_2$(CO)$_4$(*t*-Bu-DAB)$_2$ (8c). A heptane solution (20 mL) of **1c** (0.4 mmol) and *t*-Bu-DAB (1 mmol) was heated at reflux for 16 h. Cooling the reaction mixture to room temperature resulted in the formation of a yellow precipitate. This solid was then chromatographed on a silica column, first employing toluene and then dichloromethane/THF (2:1) as the eluent. The toluene fraction contained **8c**. Recrystallization from toluene afforded yellow crystals of **8c** in ca. 20% yield. Anal. Found (calcd) for C$_{24}$H$_{40}$N$_4$O$_4$Ru$_2$: C, 43.98 (44.30); H, 6.07 (6.20); N, 8.27 (8.61). ^{1}H NMR of **8c** (δ in ppm relative to internal Me$_4$Si, CDCl$_3$, 293 K, 100 MHz): 1.04, 1.43 (18 H, 18 H, s, s, *t*-Bu); 4.28 (2 H, d, J = 2.5 Hz, η^2-N=CH); 8.35 (2 H, d, J = 2.5 Hz, σ-N=CH). From the yellow dichloromethane/THF fraction **7c** was obtained in a yield of about 60%.

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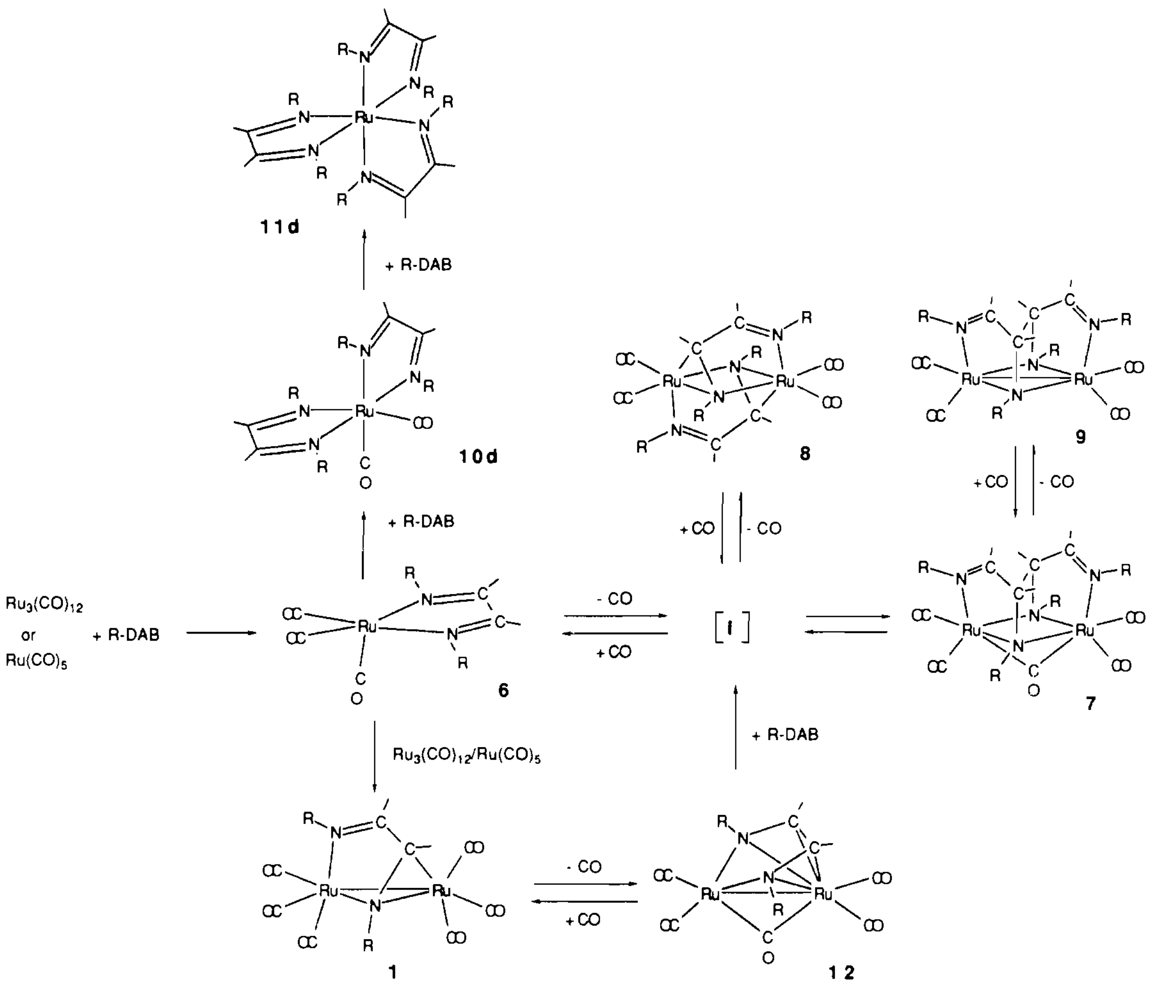
Scheme I. Observed Interconversions between Complexes in the $Ru_m(CO)_n$/R-DAB System, Together with the Proposed Intermediacy of I



Reactions of $Ru_2(CO)_4$(R-ADA) (9). Thermal Decomposition. A xylene solution (30 mL) of **9a–c** (0.4 mmol) was refluxed for 72 h. According to IR spectroscopy, a small percentage of the starting material had decomposed into products of unknown nature. No formation of **8a–c** for any of the R groups involved was observed.

Under CO. Method i. A THF solution (30 mL) of **9a–c** (0.1 mmol) was placed under an atmosphere of CO and stirred for 1 day on the window ledge at room temperature. After this period IR spectroscopy revealed the presence of **7a–c**. The products could be isolated according to published procedures[7a] in high yields (>90%).

Method ii. A toluene solution (40 mL) of **9a,b** (0.1 mmol) was refluxed under an atmosphere of CO for 8 h. Soon after reflux temperature was reached, the initial yellow color changed to red. After the reaction was stopped IR spectroscopy indicated the presence of **6a,b** as the main component together with a small amount of **1a,b**, respectively. Due to the extreme reactivity of **6a,b** (vide infra), these complexes could not be isolated.

Method iii. When the reaction was carried out in refluxing xylene (30 mL) with 1 mmol of **6a,b** in the presence of a small amount of CO (1 mL of CO in a 250-mL sealed Schlenk tube) for a period of 16 h, **8a,b** were formed, which could be isolated in nearly quantitative yields (>90%), as described before.[7a]

Crystallization of $Ru_2(CO)_5$(*i*-Pr-ADA) (7a). A benzene solution (10 mL) containing 200 mg of **7a** was converted into **6a** by method ii, as described above. The solution was degassed (to remove excess CO) and filtered, affording a bright, intensive red solution, which was placed on the window ledge. Over a period of 2 days regularly shaped orange/red crystals of **7a** had formed, which were suitable for X-ray diffraction.

Crystal Structure Determination of [$Ru_2(CO)_5$(*i*-Pr-ADA)] (7a) ($C_{21}H_{32}N_4O_5Ru_2$; Pentacarbonyl[(σ-*N*,σ-*N*′,μ-*N*″,μ-*N*‴)-*N*″,*N*‴,1,6-tetraisopropyl-1,6-diazahexa-1,5-diene-3,4-diaminato]diruthenium). Crystal data and numerical details of $C_{21}H_{32}N_4O_5Ru_2$ are listed in Table I. X-ray data were collected on an Enraf-Nonius CAD4F diffractometer (20 °C, θ–2θ scan). Reflections with an intensity below the $2.5\sigma(I)$ level were treated as unobserved. The structure was solved by means of the heavy-atom method. The refinement proceeded through block-diagonal least-squares calculations, anisotropic for Ru, C, N, and O and isotropic for H. The H atoms were introduced at their calculated positions. An empirical absorption correction (DIFABS)[15] was applied. The calculations were performed with XRAY76,[16] the atomic scattering factors were taken from Cromer and Mann,[17] and the dispersion correction factors of Ru were taken from ref 18.

Table I. Crystallographic Data for **7a**

chem formula	$C_{21}H_{32}N_4O_5Ru_2$	V	2433.9 (7) $Å^3$
		Z	4
fw	623.69	ρ_{calc}	1.70 g cm^{-3}
space group	$P2_1/a$	μ(Mo Kα)	12.5 cm^{-1}
a	20.735 (6) Å	T	20 °C
b	15.847 (4) Å	λ(Mo Kα)	0.71069 Å (Zr filtered)
c	8.034 (2) Å	final R	0.054
β	100.25 (3)°		

Results

The formation of $Ru(CO)_3$(R-DAB) (**6**) has been achieved by employing one of the methods (eqs 1–3) described below. The method to be used in order to obtain this mononuclear compound strongly depends on the substituent R at the nitrogen atoms of the R-DAB ligands. Due to their extreme reactivity (vide infra) the $Ru(CO)_3$(R-DAB) compounds could only be obtained in solution. Despite this reactivity, unambiguous characterization of these mononuclear compounds has been achieved by combined IR, FD mass, ^1H NMR, and ^{13}C NMR spectroscopy (Tables

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Table II. IR and FD Mass Data for $Ru(CO)_3(R\text{-}DAB)$ (**6**), $Ru_2(CO)_5(R\text{-}ADA)$ (**7**), $Ru_2(CO)_4(R\text{-}DAB)_2$ (**8**), $Ru_2(CO)_4(R\text{-}ADA)$ (**9**), $Ru(CO)_2(R\text{-}DAB)_2$ (**10**), and $Ru(R\text{-}DAB)_3$ (**11**) (R = *i*-Pr (**a**), c-Hex (**b**), *t*-Bu (**c**), *p*-Tol (**d**))

compd	solv/ temp	ν(CO), cm^{-1}				M[a]
6a	*b*	2040 (s)	1967 (s, br)			325 (325)
6a	*c*	2040 (s)	1967 (s)	1962 (m, sh)		
6b	*b*	2038 (s)	1965 (s, br)			405 (405)
6c	*b*	2033 (s)	1960 (s, br)			*d*
6d	*b*	2056 (vs)	1989 (s)	1977 (s)		421 (421)
7a–c[e]						
7d	*f*	2039 (m)	2010 (s)	1960 (s)	1713 (w)	*g*
8a,b,d[e]						
8c	*f*	1974 (s)	1904 (m)			650 (650)
9a,b[e]						
9c	*f*	1982 (vs)	1942 (s)	1892 (s)		650 (650)
10d	*b*	2041 (s)	1980 (vs)			629 (629)
11d						810 (809)

[a] Observed (calculated) masses of the molecular ion (*m/e*); the M values are based upon the ^{101}Ru isotope. [b] In hexane/room temperature. [c] In heptane/183 K. [d] Not measured. [e] See ref 7a. [f] In dichloromethane/room temperature. [g] Only decomposition products were observed.

II–IV), which will be discussed.

The molecular structure of $Ru_2(CO)_5$(*i*-Pr-ADA) (**7a**) has been solved. This complex contains two reductively C–C-coupled *i*-Pr-DAB ligands and is a synthetic precursor of $Ru(CO)_3$(*i*-Pr-DAB) (**6a**). Thermally or photochemically complex **6a** converts into **7a** and CO. Low-temperature photolysis of **6a** resulted in the formation of a deep purple complex (I), which is proposed to be an intermediate in the reversible conversion of **6a** into **7a**. Spectroscopic data for I have been obtained.

The present study has provided a more detailed knowledge concerning reactions between $Ru_m(CO)_n$ species and R-DAB and the interconversions between R-DAB and R-ADA complexes. An overview of the interconversions in the $Ru_m(CO)_n$/R-DAB system that will be discussed in this paper is given in Scheme I. There are several factors influencing individual steps of the $Ru_m(CO)_n$/R-DAB system, i.e. the influence of the R group, the reaction temperature, and the ratio $Ru_3(CO)_{12}$:R-DAB, which have partly been discussed before.[7,19] Light has been found to induce or influence several interconversions (**6d** → **8d**; **6a–c** → **7a–c**; **7a–c** ⇌ **9a–c**; **6d** → **10d** → **11d**), and CO plays a crucial role in the interconversions between several complexes; equilibria exist between complexes depending on the presence of CO (**1a,b** ⇌ **12a,b**; **6a,b,d** ⇌ **7a,b,d**; **6d** ⇌ **8d**; **7a–c** ⇌ **9a–c**), and a catalytic amount of CO is necessary for the isomerization of **9a** or **9b** into **8a** or **8b**, respectively.

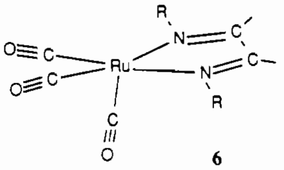
Discussion

Formation of $Ru(CO)_3(R\text{-}DAB)$. i. Reaction of $Ru(CO)_5$ with R-DAB. When ca. 0.2 mmol of $Ru(CO)_5$ is reacted with a large excess of R-DAB (ca. 4 mmol; R = *i*-Pr (**a**), c-Hex (**b**), *t*-Bu (**c**), *p*-Tol (**d**)) during 8 h at room temperature in hexane under the exclusion of light, a red (**a,b,d**) or purple (**c**) solution is obtained. IR spectroscopy (see Table II) in the ν(CO) region revealed the presence of **6a–d** together with, depending on the R group, small amounts of dinuclear $Ru_2(CO)_6(R\text{-}DAB)$ (**1**; for **a** and **b** ca. 5%, for **c** ca. 20%, and for **d** 0%). Also an absorption band at 1752 cm^{-1} was present due to an unidentified product, possibly an ester, lactone, or (cyclic) ketone. The formation of imidazolone (IR (hexane): 1689 cm^{-1}), which was formed during reactions of $Fe_2(CO)_9$ with R-DAB,[20] could be excluded in the present case.

The excess of R-DAB used, necessary to suppress the formation of **1a–c** (eq 1b), could easily be removed by washing the hexane solution twice with an aqueous 0.1 M HCl solution.

$$Ru(CO)_5 + R\text{-}DAB \rightarrow \underset{\mathbf{6}}{Ru(CO)_3(R\text{-}DAB)} + 2CO \quad (1a)$$

$$\mathbf{6} + Ru(CO)_5 \rightarrow \underset{\mathbf{1}}{Ru_2(CO)_6(R\text{-}DAB)} + 2CO \quad (1b)$$



6

Figure 3. Molecular structure of $Ru(CO)_3(R\text{-}DAB)$ (**6**).

Solutions of **6** prepared via method i are not very suitable to be applied to synthetic purposes, due to the presence of undesired byproducts.

ii. Reaction of $Ru_2(CO)_5(R\text{-}ADA)$ (7) with CO. Heating a heptane, benzene, or toluene solution containing **7** (0.2 mmol; R = *i*-Pr (**a**), c-Hex (**b**)) under an atmosphere of CO at 90 °C for ca. 15 min causes fission of the central C–C bond between the two R-DAB ligands and degradation of the dinuclear species with formation of mononuclear **6a,b**, respectively, in nearly quantitative yields. The concentration of **7**, however, should not exceed 0.5 mmol/100 mL, otherwise the concentration of CO present in solution at 90 °C will not be sufficient in order to shift the equilibrium depicted in eq 2 to the right completely. Furthermore,

$$\underset{\mathbf{7}}{Ru_2(CO)_5(R\text{-}ADA)} + CO \rightleftharpoons \underset{\mathbf{6}}{2Ru(CO)_3(R\text{-}DAB)} \quad (2)$$

long reaction times should be avoided since otherwise some disproportionation (with formation of **1a,b**) will take place. Under similar conditions **7c** (R = *t*-Bu) appeared to be stable and no formation of **6c** was observed, while for **7d** (R = *p*-Tol) conversion was completed within a few minutes at room temperature.

iii. Reaction of $Ru_2(CO)_4(R\text{-}DAB)_2$ (8) with CO. When a hexane or benzene solution (suspension) of **8d** (R = *p*-Tol), containing two bridging 6e-donating σ-N,μ_2-N′,η^2-C=N′-coordinated *p*-Tol-DAB ligands, was placed under an atmosphere of CO and stirred at room temperature, a slow degradation reaction took place yielding **6d** (eq 3). Complete transformation took about

$$\underset{\mathbf{8}}{Ru_2(CO)_4(R\text{-}DAB)_2} + 2CO \rightleftharpoons \underset{\mathbf{6}}{2Ru(CO)_3(R\text{-}DAB)} \quad (3)$$

2 days. When the reaction temperature was raised to 60 °C, the formation of **6d** was completed within 10 min. During this reaction the two η^2-coordinated imine moieties, which hold together this dinuclear species, are substituted by two CO ligands and two mononuclear fragments are formed. When **8a** (R = *i*-Pr) was used as the starting material, more drastic conditions were required for the conversion into **6a**: reflux under a CO atmosphere in xylene (bp = 144 °C) for about 2 h led only to an incomplete conversion (ca. 20%). Prolonged heating not only resulted in a slow continuation of the formation of **6a** but also caused disproportionation resulting in the formation of **1a**.

Both $Ru_2(CO)_5$(R-ADA) (**7a,b**) and $Ru_2(CO)_4$(*p*-Tol-DAB)$_2$ (**8d**) are air stable in the solid state and can easily be prepared in high yields.[7a] This makes them excellent precursors for the

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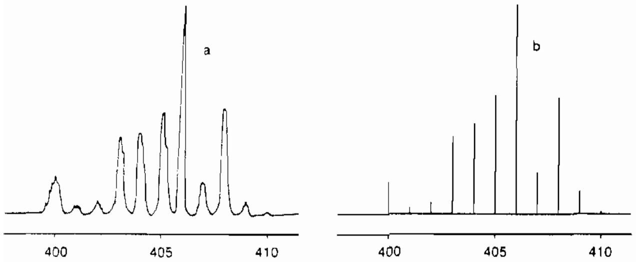

Figure 4. Observed (a) and calculated (b) mass spectra of Ru(CO)$_3$(c-Hex-DAB) (**6b**).

synthesis of Ru(CO)$_3$(R-DAB) (**6a,b,d**).

IR Spectroscopy. IR spectra of the presented Ru(CO)$_3$(R-DAB) complexes in hexane or heptane show two (R = *i*-Pr (**6a**), c-Hex (**6b**), *t*-Bu (**6c**)) or three (R = *p*-Tol) intense absorptions in the ν(CO) region (1600–2200 cm^{-1}; see Table II). This is indicative of local C_s symmetry of the Ru(CO)$_3$ unit in the case of the *p*-Tol-DAB derivative. In Figure 3 the molecular structure of **6** is shown. The depicted square-pyramidal geometry has also been found for Fe(CO)$_3$(2,6-(*i*-Pr)$_2$C$_6$H$_3$-DAB) by X-ray crystallography.[21] It should be noted, however, that for a number of Fe(CO)$_3$(α-diimine) complexes of which the X-ray structures have been determined the geometries range from square-pyramidal via intermediate structures to trigonal-bipyramidal depending on the σ-donor/π-acceptor properties of the α-diimine ligand involved.[22]

The symmetry of the Ru(CO)$_3$ unit in the case of the alkyl R groups merits some discussion. For a compound of C_s symmetry three absorption bands are expected in the ν(CO) region. Since only two are observed, a pseudo-C_{3v} symmetry seems more likely. Closer examination of the broad 1967-cm^{-1} band of Ru(CO)$_3$(alkyl-DAB), however, shows that its shape is asymmetric. Lowering the temperature stepwise from 20 to −70 °C leads to a gradual sharpening of this band into two components, a strong band at 1967 cm^{-1} and a well-resolved shoulder of medium intensity at 1962 cm^{-1}. Similar effects have been observed for the corresponding iron compounds[21,23] and can be interpreted by assuming C_s symmetry of the Ru(CO)$_3$ unit. However, the two low-frequency CO-stretching modes nearly coincide and are only well resolved at low temperatures, which means that the deviation from pseudo-C_{3v} symmetry is only small. Coalescence of the two low-frequency bands, as was found to occur in some (η^4-diene)-Fe(CO)$_3$ complexes by Grevels et al.[24] and was ascribed to a CO site exchange process that is fast on the IR time scale, seems less likely in the present case, since no real coalescence is observed. For the Ru(CO)$_3$(alkyl-DAB) complexes a slight sharpening of the low-frequency absorption bands is observed, as is usual upon lowering the temperature. The higher ν(CO) frequencies for R = *p*-Tol are in agreement with the better π-accepting properties of R-DAB ligands containing aromatic R groups compared to those containing aliphatic R groups.

FD Mass Spectroscopy. In this study, FD mass spectroscopy appeared to be an excellent tool for the identification of the mononuclear species for which elemental analysis was precluded due to their instability in solid state (vide infra). Good care was taken to avoid oxidative decomposition of the extremely air-sensitive compounds during the sampling period. The obtained spectra were successfully compared to calculated spectra, all showing the expected isotopic pattern (see Figure 4). The results are summarized in Table II.

NMR Spectroscopy. The ^{1}H NMR and ^{13}C NMR data of Ru(CO)$_3$(R-DAB) (**6**) are listed in Tables III and IV, respectively.

Table III. ^{1}H NMR Data for Ru(CO)$_3$(R-DAB) (**6**)[a]

compd	imine H[b]	R group[b]
Ru(CO)$_3$(*i*-Pr-DAB)[c] (**6a**)	7.08 (s, 2 H)	4.25 (sept,[d] 2 H), 1.27 (d,[d] 6 H)
Ru(CO)$_3$(c-Hex-DAB)[c] (**6b**)	7.09 (s, 2 H)	3.91 (m, 2 H), 2–1 (br, 20 H)
Ru(CO)$_3$(*p*-Tol-DAB)[e] (**6d**)	7.15 (s, 2 H)	7.28 (d,[f] 4 H), 6.80 (d,[f] 4 H), 2.09 (s, 6 H)

[a] The values (δ in ppm relative to TMS) have been measured in C$_6$D$_6$, at 20 °C and 100 MHz. [b] s = singlet, d = doublet, sept = septet, m = multiplet, and br = broad. [c] Prepared in situ by method ii (see Experimental Section). [d] J = 6.5 Hz. [e] Prepared in situ by method iii (see Experimental Section). [f] J = 8.5 Hz.

Table IV. ^{13}C NMR Data for Ru(CO)$_3$(R-DAB) (**6**)[a]

compd	imine C	R group	CO's
Ru(CO)$_3$(*i*-Pr-DAB)[b] (**6a**)	139.0	65.3, 26.9	204.0
Ru(CO)$_3$(c-Hex-DAB)[b] (**6b**)	139.4	74.1, 38.2, 26.6, 26.1	204.2
Ru(CO)$_3$(*p*-Tol-DAB)[c] (**6d**)	140.8	155.3, 136.4, 130.7, 124.0 (d)	200.8

[a] δ values in ppm, relative to TMS, in toluene-d_8 at −50 °C. [b] 25.2 MHz; prepared in situ by method ii (see Experimental Section). [c] 62.9 MHz; prepared in situ by method iii (see Experimental Section). [d] The *p*-tolyl methyl resonance was obscured by toluene-d_8 resonances.

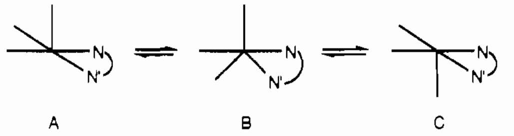

Figure 5. Proposed dynamic process taking place in **6a** via Berry pseudorotations, showing the interconversion of the faces of the R-DAB ligand.

The imine protons of **6a** appear as a singlet at about 7.1 ppm, which value is within the limits of 7–9 ppm commonly observed for chelating σ-N,σ-N'-coordinated R-DAB ligands.[25] The imine carbon atoms absorb near 140 ppm, which value is somewhat lower compared to the free ligand value of 159.6 ppm.[26] A similar shift has been found in the corresponding iron complexes,[26] while also for Ru$_2$(CO)$_5$[*i*-Pr-DAB)(MeC$_2$N(Et)$_2$]][27] and FeRu(CO)$_5$(R-DAB)(C$_3$H$_4$),[28] both containing an R-DAB ligand σ-N,σ-N'-coordinated to ruthenium, somewhat lower imine carbon shifts have been observed at 145–150 ppm.

The three CO ligands in **6a,b,d** give rise to one sharp ^{13}C signal in toluene-d_8 at −50 °C, whereas, on the basis of the C_s symmetry of **6**, two signals in a 2:1 ratio would be expected. Obviously, a dynamic process involving scrambling of the three CO's takes place, which process is fast on the NMR time scale at 25.2 MHz (**6d**: 62.9 MHz) at −50 °C. Also in Fe(CO)$_3$(R-DAB) (**3**) scrambling of the CO groups has been observed.[26] The ^{13}C signal of the CO ligands of **6d** at 200.8 ppm has been found at a somewhat lower δ value compared to those of **6a,b** at 204.0 and 204.2 ppm, respectively. This is in agreement with the observed trend in (L-L)Fe(CO)$_3$ compounds that the ^{13}CO signals shift to lower frequency with increasing π-acceptor capacity of the bidentate (L-L) ligand.[29] The ^{13}CO chemical shift of **6d** is comparable to the Ru(CO)$_5$ value (200.4 ppm)[30] and somewhat higher when compared to Ru(CO)$_3$(η^4-butadiene) (198.0 ppm).[31]

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Table V. Fractional Coordinates of the Atoms of **7a** and Equivalent Isotropic Thermal Parameters (Esd's in Parentheses)

atom	x	y	z	U_{eq}, Å^2
Ru(1)	0.05769 (6)	0.26173 (8)	0.32552 (14)	0.0435 (6)
Ru(2)	0.17801 (7)	0.17440 (8)	0.45049 (15)	0.0481 (7)
N(1)	0.2337 (7)	0.1098 (9)	0.2674 (16)	0.070 (9)
N(2)	0.1540 (5)	0.2592 (7)	0.2396 (13)	0.041 (6)
N(3)	0.0875 (6)	0.1351 (7)	0.2842 (13)	0.045 (7)
N(4)	0.0102 (5)	0.2493 (9)	0.0457 (13)	0.053 (7)
C(1)	−0.0172 (9)	0.2434 (11)	0.4207 (19)	0.072 (12)
C(2)	0.0450 (8)	0.3775 (11)	0.3632 (20)	0.061 (11)
C(3)	0.1174 (7)	0.2465 (10)	0.5526 (16)	0.050 (8)
C(4)	0.2496 (11)	0.2306 (11)	0.5783 (23)	0.091 (13)
C(5)	0.1856 (10)	0.0963 (10)	0.6217 (20)	0.071 (12)
C(6)	0.2164 (9)	0.1441 (11)	0.1206 (25)	0.082 (13)
C(7)	0.1498 (10)	0.2008 (11)	0.0975 (18)	0.075 (12)
C(8)	0.0975 (7)	0.1384 (9)	0.1032 (18)	0.049 (9)
C(9)	0.0393 (7)	0.1847 (13)	−0.0089 (19)	0.072 (11)
C(10)	0.2925 (10)	0.0551 (12)	0.2783 (23)	0.089 (15)
C(11)	0.2715 (11)	−0.0339 (13)	0.3196 (30)	0.110 (18)
C(12)	0.3439 (13)	0.0841 (17)	0.4173 (42)	0.166 (26)
C(13)	0.1893 (7)	0.3389 (9)	0.2243 (18)	0.052 (9)
C(14)	0.2603 (11)	0.3245 (11)	0.1993 (31)	0.106 (17)
C(15)	0.1536 (9)	0.3988 (9)	0.0931 (21)	0.065 (11)
C(16)	0.0500 (9)	0.0593 (9)	0.3259 (23)	0.064 (11)
C(17)	−0.0197 (9)	0.0547 (12)	0.2207 (25)	0.082 (13)
C(18)	0.0844 (11)	−0.0218 (11)	0.3190 (23)	0.093 (14)
C(19)	−0.0440 (7)	0.2875 (12)	−0.0670 (21)	0.070 (12)
C(20)	−0.0251 (12)	0.3718 (17)	−0.1145 (32)	0.131 (21)
C(21)	−0.1045 (11)	0.2844 (25)	0.0182 (27)	0.179 (27)
O(1)	−0.0583 (6)	0.2269 (8)	0.4897 (16)	0.092 (10)
O(2)	0.0397 (7)	0.4476 (8)	0.3837 (19)	0.105 (11)
O(3)	0.1140 (6)	0.2702 (8)	0.6910 (13)	0.083 (9)
O(4)	0.2924 (7)	0.2665 (9)	0.6587 (19)	0.122 (12)
O(5)	0.1852 (9)	0.509 (9)	0.7366 (16)	0.122 (12)

Table VI. Selected Bond Distances Involving Non-Hydrogen Atoms of **7a** (Å) (Esd's in Parentheses)

Ru(1)···Ru(2)	2.873 (2)	N(2)–C(7)	1.46 (2)
Ru(1)–N(2)	2.23 (1)	N(2)–C(13)	1.48 (2)
Ru(1)–N(3)	2.14 (1)	N(3)–C(8)	1.51 (2)
Ru(1)–N(4)	2.30 (1)	N(3)–C(16)	1.50 (2)
Ru(1)–C(3)	2.03 (1)	N(4)–C(9)	1.30 (2)
Ru(2)–N(1)	2.27 (1)	N(4)–C(19)	1.44 (2)
Ru(2)–N(2)	2.15 (1)	C(3)–O(3)	1.19 (2)
Ru(2)–N(3)	2.19 (1)	C(6)–C(7)	1.63 (3)
Ru(2)–C(3)	1.98 (1)	C(7)–C(8)	1.47 (2)
N(1)–C(6)	1.29 (2)	C(8)–C(9)	1.56 (2)
N1)–C(10)	1.49 (3)		

In C_6D_6 at 20 °C the methyl groups of the *i*-Pr groups in **6a** give rise to only one doublet at 1.27 ppm, whereas, on the basis of the proposed C_s symmetry, a set of two doublets might be expected. Also the ^{13}C spectrum of **6a** shows equivalent *i*-Pr methyl resonances, similar to the situation observed for Fe-$(CO)_3$(*i*-Pr-DAB) (**3a**).[26a] Therefore, ^1H NMR spectra (250.1 MHz) of **6a** have been recorded at low temperatures, using an approximately equimolar mixture of toluene-d_8/CD_2Cl_2 as the solvent. At −50 °C the *i*-Pr methyl groups are still observed as a sharp doublet. Upon further lowering of the temperature to −90 °C, no broadening of this signal, except due to increasing viscosity, is observed. The dynamic process that equilibrates the three CO ligands and the two faces of the *i*-Pr-DAB ligand, i.e. the diastereotopic methyl groups, may be visualized by Berry pseudorotations that interconvert inter alia the structures A, B, and C in Figure 5.

Molecular Structure of $Ru_2(CO)_5$(*i*-Pr-ADA). Crystals of $Ru_2(CO)_5$(*i*-Pr-ADA) (**7a**), which is the main synthetic precursor for $Ru(CO)_3$(*i*-Pr-DAB) (**6a**), suitable for X-ray diffraction were grown by slowly converting **6a** into **7a** in benzene. The molecular geometry of **7a** together with the atomic numbering is shown in Figure 6. In Tables V–VII the atomic coordinates, bond distances, and selected bond angles are given.

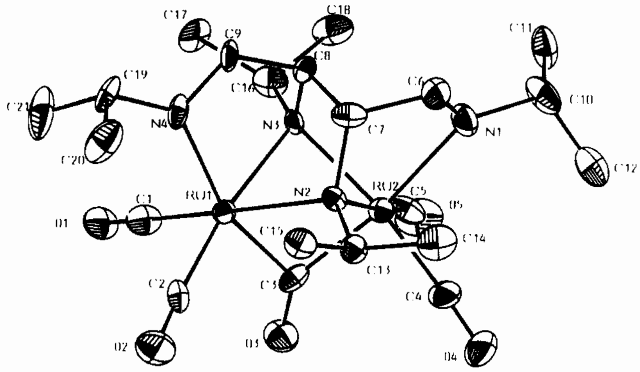

Figure 6. ORTEP diagram of $Ru_2(CO)_5$(*i*-Pr-ADA) (**7a**).

Table VII. Selected Bond Angles involving Non-Hydrogen Atoms of **7a** (deg) (Esd's in Parentheses)

Ru(2)–Ru(1)–C(3)	43.6 (4)	Ru(1)–N(2)–C(7)	108.8 (10)
N(2)–Ru(1)–N(3)	68.6 (4)	Ru(2)–N(2)–C(7)	101.1 (8)
N(2)–Ru(1)–N(4)	87.0 (4)	Ru(1)–N(3)–Ru(2)	83.2 (5)
N(2)–Ru(1)–C(3)	70.7 (5)	Ru(1)–N(3)–C(8)	102.1 (8)
N(3)–Ru(1)–N(4)	81.6 (4)	Ru(2)–N(3)–C(8)	109.2 (8)
N(3)–Ru(1)–C(3)	83.2 (5)	Ru(1)–N(4)–C(9)	104.7 (8)
N(4)–Ru(1)–C(3)	163.1 (5)	Ru(1)–N(4)–C(19)	136.7 (10)
Ru(1)–Ru(2)–C(3)	44.9 (3)	C(9)–N(4)–C(19)	118.2 (12)
N(1)–Ru(2)–N(2)	81.0 (5)	Ru(1)–C(3)–Ru(2)	91.5 (5)
N(1)–Ru(2)–N(3)	87.5 (4)	N(1)–C(6)–C(7)	115.4 (16)
N(1)–Ru(2)–C(3)	164.2 (5)	N(2)–C(7)–C(6)	119.2 (13)
N(2)–Ru(2)–N(3)	69.2 (4)	N(2)–C(7)–C(8)	110.0 (14)
N(2)–Ru(2)–C(3)	83.7 (5)	C(6)–C(7)–C(8)	103.9 (13)
N(3)–Ru(2)–C(3)	83.0 (5)	N(3)–C(8)–C(7)	106.4 (11)
Ru(2)–N(1)–C(6)	108.2 (12)	N(3)–C(8)–C(9)	110.5 (12)
Ru(2)–N(1)–C(10)	137.0 (10)	C(7)–C(8)–C(9)	99.5 (13)
C(6)–N(1)–C(10)	113.0 (15)	N(4)–C(9)–C(8)	122.2 (13)
Ru(1)–N(2)–Ru(2)	82.0 (4)		

The molecule consists of two $Ru(CO)_2$ units bridged by a CO ligand and a formally 10e-donating *i*-Pr-ADA ligand resulting from the reductive C–C coupling of two *i*-Pr-DAB ligands. As a result of this coupling, both N(2)–C(7) and N(3)–C(8), formerly imine bonds, have been reduced to aminato C–N bonds and a new bond connecting C(7) and C(8) has been formed. The molecule exhibits noncrystallographic C_2 symmetry with the 2-fold axis running through O(3), C(3), and the midpoint of C(7)–C(8) and confirms the geometry anticipated from spectroscopic measurements.[7a] The overall structure closely resembles that of Ru_2-$(CO)_5$(*i*-Pr-APE),[32] with the difference that in the APE ligand the imine bonds are part of an aromatic pyridyl ring. Owing to disorder in the APE ligand, a detailed description of the molecular structure of this compound was not justified. Now we are able to describe a representative of this class of compounds in more detail.

The internuclear distance between the two ruthenium atoms in **7a** amounts to 2.873 (2) Å, which is, unexpectedly, within the limits usually observed for single ruthenium metal–metal bonds of 2.70–2.90 Å.[33] On the basis of CVMO theory,[34] however, the presence of a metal–metal bond is not to be expected, and from UV–vis spectra recorded at different temperatures it could already be concluded that no direct metal–metal bond is present in **7a**.[7a] In this context it is interesting to note that in $Ru_2(CO)_5$(*i*-Pr-APE) a similar intermetallic distance of 2.858 (2) Å has been found. Thus, the observed short internuclear distances in **7a** and Ru_2-$(CO)_5$(*i*-Pr-APE) appear to be induced by the bridging ligands.

In other diaminato-bridged dinuclear compounds where a M–M bond is expected to be present (opposite to the case of **7a**) very short internuclear distances have been observed.[28,35] For instance

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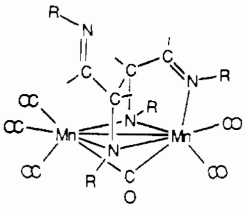


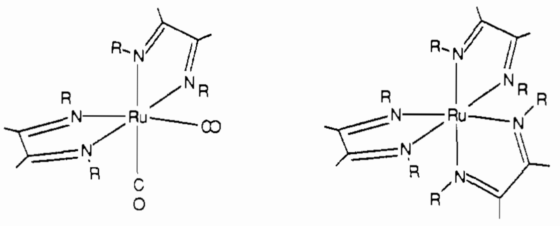
13; R = t-Bu

Figure 7. Molecular structure of $Mn_2(CO)_6$(*t*-Bu-ADA) (**13**).

the Ru–Ru bond in $Ru_2(CO)_6$[*i*-Pr-NCH_2CH_2N-*i*-Pr][35a] amounts to 2.5745 (7) Å, which is 0.3 Å shorter than that in **7a**. The Ru(1)–N(2)–Ru(2) and Ru(1)–N(3)–Ru(2) angles in **7a** amount to 82.0 (4) and 83.0 (4)°, respectively, and are somewhat larger than the M–N–M angles of 75° usually observed in diaminato-bridged dimers. Also the Ru–N(aminato) distances, which vary from 2.14 (1) to 2.23 (1) Å, are longer than in other diaminato-bridged complexes (e.g. the Ru–N distances in $Ru_2(CO)_6$[*i*-Pr-NCH_2CH_2N-*i*-Pr][35a] amount to 2.110 (5) Å (mean)). These anomalous geometrical features are a consequence of the relative long (nonbonding) Ru–Ru vector in the two Ru–N–Ru triangles present in **7a**. Unfortunately, no comparative dinuclear complexes containing a CO ligand bridging two mutual nonbonding Ru centers have been published,[36] which precludes a more detailed discussion with respect to the influence of the bridging CO ligand on the Ru–Ru distance. Thus, the Ru–Ru distance observed in **7a** arises from a delicate balance between the bridging ligands forcing the metal atoms into proximity and the electronic repulsion between the two metal centers, which has the opposite effect.

Due to the bridging CO ligand two coordination sites (one on each ruthenium atom) are opposite C(3) and are occupied by N(1) and N(4). Both N atoms are part of the ADA ligand and are attached to the ruthenium centers by rather long bonds of 2.27 (1) and 2.30 (1) Å, respectively, while usually Ru–N(imine) σ bonds of 2.10–2.15 Å are observed.[37] This points to somewhat weakened Ru–N(imine) bonds. Apparently the rigid multidentate *i*-Pr-ADA ligand prevents the imine nitrogen atoms from approaching the metal centers more closely. Interestingly, in $Mn_2(CO)_6$(*t*-Bu-ADA) (**13**; Figure 7) only one of the imine nitrogen atoms of the *t*-Bu-ADA ligand is coordinated to the metal framework and a metal–metal bond has been formed.[38]

The question whether the forced coordination of N(1) and N(4) to Ru(2) and Ru(1), respectively, induces any structural strain within the ADA ligand is interesting, since geometrical constraints might explain the facile thermal rupture of the central C(7)–C(8) bond in **7a**. The Ru–N–C angles within the two ruthenadiazacyclopentenyl rings in **7a** [Ru(1)–N(3)–C(8) = 102.1 (8)°, Ru(1)–N(4)–C(9) = 104.7 (8)°, Ru(2)–N(1)–C(6) = 108.2 (12)°, Ru(2)–N(2)–C(7) = 101.1 (8)°] are somewhat smaller than those found in complexes containing a ruthenium-coordinated chelating 4e σ-N,σ-N′ R-DAB ligand (ca. 115°)[27,28] but comparable to those in other Ru systems containing an R-DAB ligand that is C–C coupled to an organic substrate.[5,6] The C(6)–C(7)–C(8) and C(7)–C(8)–C(9) angles amount to 103.9 (13) and 99.5 (13)°, respectively, and are smaller than the optimum value of 109.47° for sp^3 hybridized atoms. This is probably a result of the forced coordination of N(1) and N(4) to the ruthenium centers.



10d; R = p-Tol 11d; R = p-Tol

Figure 8. Proposed structures of $Ru(CO)_2$(*p*-Tol-DAB)$_2$ (**10d**) and Ru(*p*-Tol-DAB)$_3$ (**11d**).

Unfortunately, a detailed discussion of the bond lengths in the spine of the *i*-Pr-ADA ligand is not justified because of the relatively large standard deviations. Although the central C(7)–C(8) bond of 1.47 (2) Å seems shorter compared to the C(6)–C(7) and C(8)–C(9) bonds of 1.63 (3) and 1.56 (2) Å, respectively, they differ hardly significantly from normal single C–C bonds of 1.54 Å, when the generally accepted uncertainty of $\pm 3\sigma$ is invoked. However, several small angles are observed in the complex (vide supra), which, together with the long Ru–N(imine) bonds, point to a forced coordination of the ADA ligand to the diruthenium fragment. Whether the facile breaking of the central C(7)–C(8) bond, which is an experimental fact, may be explained by these structural observations, however, remains open to question.

Reactivity of $Ru(CO)_3$(R-DAB). The mononuclear $Ru(CO)_3$(R-DAB) compounds discussed in this paper are extremely air sensitive, are both thermally and photochemically labile, and could not be isolated in solid state as pure samples (vide infra), precluding both analytical and crystallographic studies. The compounds are soluble and stable in most common solvents such as hexane, diethyl ether, benzene, acetone, THF, toluene, and dichloromethane. In tetrachloromethane and chloroform, however, a rapid oxidation reaction takes place. Oxidative additions to Ru^0(R-DAB) species have already been investigated and are assumed to occur in catalytic reactions (e.g. hydrosilylation).[39] Purification of the compounds from reaction mixtures by column chromatography on silica was severely hampered by decomposition. These compounds could therefore not be isolated from reaction mixtures formed during thermal reactions between $Ru_3(CO)_{12}$ and R-DAB,[19] although prepared via this method they have been successfully used as starting material for the synthesis of homo- and heterodinuclear species.[28,19] Removal of the solvent under vacuum from pure $Ru(CO)_3$(R-DAB) (**6**) solutions resulted in the (partial) formation of CO-dissociation products (vide infra). Therefore, the compounds **6** could only be obtained in solutions. These may be stored for longer periods under the exclusion of light at room temperature under an atmosphere of CO (to prevent the reverse of eqs 2 and 3) or at −80 °C.

Upon irradiation at room temperature[40] or heating of a solution of **6a–d**, prepared by one of the methods described above, **7a–c** or **8d** are formed according to the reverse of eqs 2 and 3, respectively. The observed thermal lability of **6a,b** contrasts with earlier findings,[19] where it was stated that these mononuclear compounds (after being prepared thermally from $Ru_3(CO)_{12}$ and R-DAB) were rather persistent and reacted only slowly to give **8a,b**. This seeming contradiction can be rationalized by invoking the presence of liberated CO in $Ru_3(CO)_{12}$/R-DAB reaction mixtures. The small amount of CO present in these solutions prevents the equilibrium in eq 2 from shifting to the left completely while **7a** and **7b** convert, under the conditions applied, slowly into

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(40) Irradiation of solution of **6d** at −70 °C with an Hg lamp gives **7d**, which, upon warming to room temperature, disproportionates (due to the presence of liberated CO) to give **8d**.

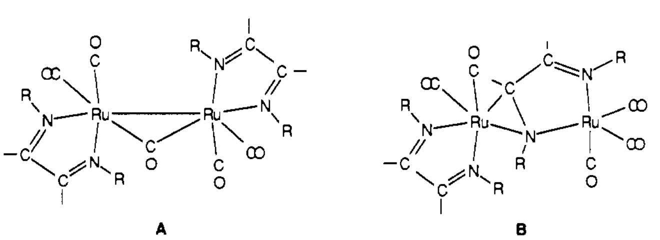

Figure 9. Proposed alternative structures for I.

8a and **8b**, respectively (eq 6). When **6a** is irradiated at -70 °C, a dark purple, almost black compound is formed in solution. On the basis of its chemical behavior, this compound is assumed to be an intermediate in the C–C coupling reaction depicted in eq 2, which will be discussed later on.

When an excess of *p*-Tol-DAB (**d**) is present during irradiation of **6d**, another reaction route is followed. When the sun is used as light source, only dark green $Ru(CO)_2(p\text{-Tol-DAB})_2$ (**10d**) is formed. Irradiating with a 200-W Hg lamp gives a mixture of **10d** and **11d** (eq 4). Probably, the more intensive Hg light source

$$\underset{\textbf{6d}}{Ru(CO)_3(p\text{-Tol-DAB})} + \underset{\textbf{d}}{p\text{-Tol-DAB}} \xrightarrow{h\nu} \underset{\textbf{10d}}{Ru(CO)_2(p\text{-Tol-DAB})_2} + \underset{\textbf{11d}}{Ru(p\text{-Tol-DAB})_3} \quad (4)$$

accelerates substitution of the CO ligands in **10d**. These new mononuclear compounds are not formed when the R-DAB ligand contains aliphatic R groups.

The IR spectrum of **10d** shows two strong absorptions in the ν(CO) region, clearly indicating a cis arrangement of the two CO ligands in this novel, dark green, 20e complex. The proposed structures of the extremely air-sensitive compounds **10d** and **11d** are shown in Figure 8. The existence of a 20e six-coordinate center in such complexes has previously been substantiated by X-ray crystallography for $Ru(\text{anisyl-DAB})_3$.[41] The relevance of this type of compounds can be illustrated with the $[Ru(bpy)_2(CO)_2]^{2+}$-catalyzed electrochemical reduction of CO_2, which is proposed[42] to proceed via the intermediacy of $[Ru(bpy)_2(CO)_2]^0$, a formally 20e compound closely related to **10d**.

When the solvent was removed under vacuum, **6** reacts according to the reverse of eq 2. Interestingly, the formerly inaccessible complex **7d** could also be obtained via this route. Probably, the reactivity of CO toward **7d** (vide supra) precluded its isolation from thermal reactions of $Ru_3(CO)_{12}$ with *p*-Tol-DAB. With the isolation of **7d** it has now become clear that ADA formation is not restricted to alkyl-DAB ligands. The IR and ^1H NMR data of this new compound are comparable to those of other $Ru_2(CO)_5(R\text{-}ADA)$ (**7**) compounds and are included in Table II (IR) and the Experimental Section (^1H NMR).

Intermediate in the C–C Coupling/Fission Reaction. Irradiating a red solution of **6a** in toluene with a Hg lamp at -70 °C for a few minutes results in the formation of a deep purple, almost black solution. When this solution is degassed to remove liberated CO and is then slowly warmed up to -20 °C, a yellow solution of **7a** is obtained. Upon saturation of the deep purple solution with CO and increase of the temperature to -20 °C, a red solution containing mainly **6a** and furthermore some **7a** is obtained. These observations are best explained by assuming the occurrence of intermediate I with stoichiometry $Ru_2(CO)_5(i\text{-Pr-DAB})_2$, which is formed via elimination of a CO ligand from the parent **6a** and subsequent reaction of the highly reactive 16e $Ru(CO)_2(i\text{-Pr-DAB})$ fragment with a second molecule of **6a**. The intense color indicates that I contains at least one chelating *i*-Pr-DAB ligand. From this intermediate two different thermal reaction paths are accessible, the actual path depending on whether CO is present or not.

Two structures may be considered for this intermediate (see Figure 9). First, a symmetric metal–metal-bonded species (A), containing a bridging CO ligand and two chelating R-DAB ligands, can be envisaged. Credibility for this structure stems from the formation of similar compounds when $Fe(CO)_3(R\text{-}DAB)$ (**3**) or $Ru(CO)_3[(i\text{-Pr})_2CH\text{-}DAB]$ are irradiated at low temperature (150 K) in *n*-pentane.[43] Warming this solution of $M_2(CO)_5(R\text{-}DAB)_2$ (M = Fe, Ru) without liberated CO being removed, however, does not lead to the formation of $M_2(CO)_5(R\text{-}ADA)$ but to the re-formation of $M(CO)_3(R\text{-}DAB)$. This is in line with (i) the fact that neither $Fe_2(CO)_5(R\text{-}ADA)$ nor $Ru_2(CO)_5[(i\text{-Pr})_2CH\text{-}ADA]$ have ever been synthesized and (ii) the observed reactivity of $Ru_2(CO)_5(i\text{-Pr-DAB})_2$ toward CO (vide supra). Alternatively, the crucial purple intermediate I may be an asymmetric species (B) containing both a 6e-donating R-DAB and a 4e-donating R-DAB. A similar intermediate has been proposed for the formation of $Ru_2(CO)_5(R\text{-}APE)$ from $Ru_2(CO)_4(R\text{-}Pyca)_2$ and CO.[44] This structure is in keeping with the hypothesis that η^2-C=N coordination is a necessary condition to induce C–C coupling reactions in dimeric $Ru_2(CO)_6(R\text{-}DAB)$ and $FeRu(CO)_6(R\text{-}DAB)$ complexes.[5,45]

Low-temperature photolysis experiments have been carried out in order to obtain spectroscopic data of I. Irradiation into the high-energy slope of the MLCT band[43a] of **6a** in heptane solution at -70 °C (λ_{max}(**6a**) = 482 nm) by using the 458-nm line of an Argon ion laser (power 10 mW) was performed, and UV and IR spectra were recorded at regular intervals. At least two stages could be discerned. During the first stage the intensity of the 482-nm band in the UV spectrum of **6a** gradually decreased and a new band was observed at λ_{max} = 688 nm. During the second process the remainder of the 482-nm band and the new 688-nm band both disappeared and two new bands were observed at 380 and 570 nm. Upon further irradiation these latter bands slowly disappeared again. At all stages of irradiation, warming of the solutions to ambient temperature gave **6a** and/or **7a**.

FT-IR spectra of the primary photoproduct show four absorptions in the terminal region (2004 (w), 1970 (vs), 1954 (m), and 1917 (m) cm^{-1}) and one in the bridging region (1752 (m) cm^{-1}). Although these IR data are in accordance with structure A, and comparable to those observed for $Ru_2(CO)_5[(i\text{-Pr})_2CH\text{-}DAB]_2$,[43] the conclusion that A is the *only* intermediate from which the thermal C–C coupling reaction may take place is not justified, since this species was only obtained in a low (steady state) concentration, whereas other species were formed as well upon prolonged irradiation. IR spectra of the sample at later stages, however, were too complicated to interpret unambiguously, so accurate IR data of the secondary photoproduct(s) could not be obtained. Extended photochemical studies are necessary in order to obtain detailed insight into the reaction pathway by which **7a** is formed out of **6a**.

We propose that I is also an intermediate in the C–C decoupling reaction (**7a,b,d** → **6a,b,d**). Complex I might well be in thermal equilibrium with the parent R-ADA compound **7**. This proposal is supported by the observation that a solution of **7a,b**, upon heating in toluene or xylene, becomes dark red, which is unexpected since the colors of all known products possibly being formed (**8** and **9**) and of **7** itself range from yellow to orange. The intense color might stem from the presence of a small amount of I, which is in equilibrium with **7a,b**. In agreement with this conjecture, a solution of **7c** in xylene remains yellow upon heating and no products arising from C–C fission are formed from **7c**. The facile fission of the central C–C bond in **7a** might be ascribed to the presence of some structural strain in the spine of the ADA ligand,

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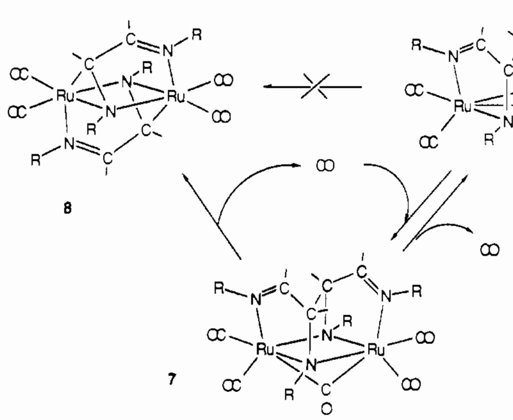
Scheme II. CO-Catalyzed Isomerization of $Ru_2(CO)_4$(R-ADA) (**9a**,**b**) to $Ru_2(CO)_4(R\text{-}DAB)_2$ (**8a**,**b**) (R = *i*-Pr (**a**), c-Hex (**b**))



as discussed in the molecular structure section. Furthermore, since in the proposed structure of I both ruthenium atoms obey the 18e rule and only a small structural reorganization is required for the conversion of **7a** into I, a low kinetic barrier for this conversion will facilitate fission of the central C–C bond in **7a**.

The proposed reversible C–C bond fission/formation reaction has a precedent in, for instance, the photochemical breaking of the connective C–C bond in $Mo_2(CO)_6$(R-ADA) with formation of $Mo_2(CO)_6(R\text{-}DAB)_2$, containing two bridging 6e-donating R-DAB ligands.[46] In that case, $Mo_2(CO)_6$(R-ADA) was formed again in a thermal reaction. Also, the C–C connective bond between two R-Pyca ligands in $Ru_2(CO)_5$(R-APE) could be ruptured thermally with formation of $Ru_2(CO)_4(R\text{-}Pyca)_2$ and could be restored in a reaction of the latter with CO.[44]

Reactions of $Ru_2(CO)_n$(R-ADA) (n = 4, 5). When heated in toluene at reflux (110 °C) or irradiated in THF at room temperature, **7a–c** loses a CO ligand (eq 5). For R = *t*-Bu (**7c**) only

$$\underset{\mathbf{7}}{Ru_2(CO)_5(\text{R-ADA})} \rightleftharpoons \underset{\mathbf{9}}{Ru_2(CO)_4(\text{R-ADA})} + CO \qquad (5)$$

the photochemical reaction gave good yields (>80%) of **9c**. Compound **7c** appeared to be thermally very stable, in line with earlier observations.[7a]

When a xylene solution of **7a**,**b** is refluxed (144 °C), a different reaction takes place (eq 6). Apart from CO dissociation also

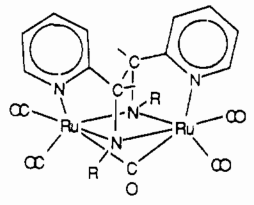
$$\underset{\mathbf{7}}{Ru_2(CO)_5(\text{R-ADA})} \rightarrow \underset{\mathbf{8}}{Ru_2(CO)_4(\text{R-DAB})_2} + CO \qquad (6)$$

rupture of the central C–C bond of the R-ADA ligand has occurred. Under similar conditions for R = *t*-Bu no conversion takes place.

To explain the different products formed in eqs 5 and 6, respectively, it has tentatively been suggested that **9** was an intermediate in the formation of **8**.[7a] However, we have now found that when a xylene solution of pure **9** is refluxed, no isomerization into **8** takes place, not even after 120 h. When the same reaction is carried out in a sealed Schlenk tube in the presence of a very small amount of added CO (0.04 equiv), however, **8a**,**b** are formed in nearly quantitative yields within 16 h (eq 7). In this conversion CO acts as a catalyst for the fission of a C–C bond.

$$\underset{\mathbf{9}}{Ru_2(CO)_4(\text{R-ADA})} \xrightarrow{[CO]} \underset{\mathbf{8}}{Ru_2(CO)_4(\text{R-DAB})_2} \qquad (7)$$

Reaction of **9a**,**b** in refluxing toluene in a CO atmosphere resulted in the formation of **6a**,**b**, respectively. At room temperature **9a–c** react slowly with CO according to the reverse of eq 5 with formation of **7a–c**. This reaction, in which a metal–metal bond is broken, is considerably accelerated by solar light. The above mentioned reactions clarify why a (small) amount of CO is necessary for the isomerization of **9a**,**b** into **8a**,**b**, although it is not being consumed. Apparently, the formation of **8a**,**b** from **9a**,**b** proceeds via the reverse of the reaction depicted in eq 5, with the intermediacy of **7a**,**b**, respectively, which compounds can only be formed when CO is present. The corresponding catalytic cycle, invoking **7**–**9** and CO is shown in Scheme II and constitutes the top right section of Scheme I.



14; R = t-Bu

Figure 10. Molecular structure of $Ru_2(CO)_5$(*t*-Bu-APE) (**14**).

For R = *t*-Bu no formation of **8c** or **6c** could be induced starting from **9c**. In this case the reaction with CO stopped at the stage of **7c**. It has already been shown that **7c** does not react with CO to give **6c** and that it is not possible to convert **7c** thermally into **8c** (vide supra). Apparently, the bulky *t*-Bu group has a stabilizing effect on the C–C bond connecting the two *t*-Bu-DAB ligands in **7c**. By use of a different reaction route, however, the formerly inaccessible **8c** could be obtained in low yield (ca. 20%; eq 8).

$$\underset{\mathbf{1c}}{Ru_2(CO)_6(t\text{-Bu-DAB})} + \underset{\mathbf{c}}{t\text{-Bu-DAB}} \rightarrow$$
$$\underset{\mathbf{8c}}{Ru_2(CO)_4(t\text{-Bu-DAB})_2} + \underset{\mathbf{7c}}{Ru_2(CO)_5(t\text{-Bu-ADA})} \qquad (8)$$

The isolation of **8c** according to eq 8 demonstrates that the failure of the reaction according to eq 6 in the case of R = *t*-Bu is of kinetic rather than thermodynamic origin. Furthermore, its isolation implies that formation of R-ADA products is not a prerequisite for the formation of **8** and that there are at least two independent reaction paths operative for the formation of **8**. From these results, it is now clear that **8** can be formed either from **7** or from **1** and R-DAB, probably via the common intermediate I. As a restriction, this intermediate (hence also **8c**) is not accessible from **7c**. It should be noted that the formation of **8** from I must not necessarily proceed by elimination of a CO ligand from this dinuclear species but may also occur via the degradation of I into mononuclear species ($Ru(CO)_2$(R-DAB) and $Ru(CO)_3$(R-DAB)) and subsequent dimerization of two unsaturated 16e $Ru(CO)_2$(R-DAB) fragments. The possibility of such a sequence is corroborated by the formation of **8** during the chemical reduction of mononuclear $Ru^{II}(CO)_2(\text{R-DAB})I_2$.[47] An overview of the reactions is given in Scheme I.

A possible explanation for the stability of the C–C connective bond in **7c** is that a different process takes place when **7c** is heated in solution. Instead of the C–C bond being broken, dissociation of one of the σ-coordinated imines with concomitant formation of a metal–metal bond and a shift of the bridging CO to the metal from which the imine has been eliminated might occur. The 8e coordination mode of the *t*-Bu-ADA ligand, obtained thus, in which only one of the imine N atoms is bonded to the metal centers, has actually been observed for $Mn_2(CO)_6$(*t*-Bu-ADA) (**13**; Figure 7)[38] and might be ascribed to the bulkiness of the *t*-Bu groups, which destabilize the Ru–N(imine) bonds in **7c**. Weakening of metal–nitrogen bonds by a *t*-Bu group on the nitrogen atom is a known phenomenon.[43a] Further support for this hypothesis might be gained from the facile splitting of the central C–C bond of the *t*-Bu-APE analogue, in which the C=N functions bear no bulky *t*-Bu groups (**14**, Figure 10).[44]

The reactivity of **9** may be explained in a similar way. In this complex a Ru–Ru bond is present and therefore the intermetallic distance will be shorter than the one found in **7a**. As a consequence, the Ru–N(imine) bonds in **9** will be even less strong compared to the already weak Ru–N(imine) bonds in **7a** (see molecular structure section). Therefore, the stability of the central

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C–C bond in **9**, which prevents direct isomerization of **9** into **8** (eq 7), might be rationalized by assuming that dissociation of one of the imine nitrogen bonds from a ruthenium center in this complex is a process requiring less energy than fission of the central C–C bond and takes place reversibly when **9** is heated or irradiated. Invoking the formation of an unsaturated 16e ruthenium center also accounts for the photochemical acceleration of the uptake of a CO ligand by **9** to give **7** (reverse of eq 5).

Comparison with Reactions in the $Ru_3(CO)_{12}$/R-Pyca System. The reactions within the $Ru_m(CO)_n$/R-DAB system (Scheme I) roughly parallel those in the $Ru_3(CO)_{12}$/R-Pyca system [R-Pyca = 6-R′C_5H_3N-2-(C(H)=NR)].[2,44] In the R-Pyca case $Ru_2(CO)_4$(R-Pyca)$_2$, a complex isostructural to **8**, proved to be formed directly from $Ru_2(CO)_5$(R-APE) or from $Ru_2(CO)_6$(R-Pyca) and R-Pyca without the intermediacy of $Ru_2(CO)_4$(R-APE). This sequence also appears to be valid in the R-DAB system. Some important differences between the two systems, however, should be noted. First, $Ru(CO)_3$(R-Pyca) neither is formed during reactions of $Ru_2(CO)_4$(R-Pyca)$_2$ or $Ru_2(CO)_5$(R-APE) with CO nor has been observed as a product (or intermediate) during thermal reactions of $Ru_3(CO)_{12}$ with R-Pyca.[44] This suggests that under the applied reaction conditions $Ru(CO)_3$(R-Pyca) is even more labile than $Ru(CO)_3$(R-DAB) (**6**) with respect to CO elimination. This is in line with the observation that no formation of $Ru(CO)_3$(R-Pyca) occurs during reactions of $Ru(CO)_5$ with R-Pyca.[48] Second, the reactivity of $Ru_2(CO)_5$(R-APE) depends mainly on the substituents on the 6-positions of the pyridyl parts of the R-APE ligand and, in contrast to the corresponding R-ADA compounds, only little on the reaction temperature or the R groups on the N atoms. For the R-Pyca derivatives $Ru_2(CO)_4$(R-APE) was formed only when a methyl group was present in the 6-position. With an H atom at this position $Ru_2(CO)_4$(R-Pyca)$_2$ was the main product.

Conclusions

We have shown that, provided the correct kinetic reaction path is chosen, $Ru(CO)_3$(R-DAB) (R = *i*-Pr (**6a**), c-Hex (**6b**), *p*-Tol (**6d**)) can be obtained as a pure compound in solution, applying reversible thermal carbonylation reactions of the known complexes $Ru_2(CO)_5$(R-ADA) (**7a,b**) or $Ru_2(CO)_4$(*p*-Tol-DAB)$_2$ (**8d**). The intermediacy of complex I with stoichiometry $Ru_2(CO)_5$(R-DAB)$_2$, which could be observed in a low steady-state concentration by irradiating a solution of **6a** at low temperature (−70 °C), is proposed. The present study has provided a more detailed insight into the thermally and photochemically induced interconversions between R-DAB and R-ADA complexes in the $Ru_m(CO)_n$/R-DAB system and the crucial role of CO therein.

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Supplementary Material Available: Tables of complete crystal structure data, all bond lengths and angles, anisotropic thermal parameters of the non-hydrogen atoms, and calculated fractional coordinates and the isotropic thermal parameters of the H atoms (8 pages); a listing of the structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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(48) $Ru(CO)_5$ (ca. 0.2 mmol) and *i*-Pr-Pyca (4 mmol) in hexane were stirred at room temperature for 6 h. During this period the IR frequencies belonging to $Ru(CO)_5$ (2037 and 2002 cm^{-1}) gradually disappeared and a dark blue precipitate was formed. This product, which is insoluble in common organic solvents (dichloromethane, ether, hexane, THF), is not air sensitive and shows three broad IR frequencies in KBr (2033 (w), 1970 (s), 1902 (w) cm^{-1}). These observations clearly indicate that this product is not $Ru(CO)_3$(*i*-Pr-Pyca).

Contribution from Crystalytics Company, Lincoln, Nebraska 68501, and Departments of Chemistry, University of Nebraska, Lincoln, Nebraska 68588, and University of Illinois, Urbana, Illinois 61801

$Nb_2W_4O_{19}^{4-}$ and $P_3O_9^{3-}$ Complexes of (Cyclooctadiene)iridium(I): Synthesis, Structure, and Stability of Tetra-*n*-butylammonium Salts of $\{[(C_8H_{12})Ir]_5(Nb_2W_4O_{19})_2\}^{3-}$, $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$, and $[(C_8H_{12})Ir(P_3O_9)]^{2-}$

V. W. Day,*[,†] W. G. Klemperer,*[,‡] and D. J. Main[‡]

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Stoichiometric reaction of $[(C_8H_{12})Ir(NCCH_3)_2]PF_6$ with $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ in CH_2Cl_2 yields crystalline $\{[(C_8H_{12})Ir]_5(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_3$ (**1**). IR and $^{13}C\{^1H\}$ NMR spectroscopy indicate that the anion of **1** is isostructural with the (norbornadiene)rhodium(I) complex $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ (anion of **2**) and contains two octahedral $Nb_2W_4O_{19}^{4-}$ ions linked together in a face-to-face fashion by five four-coordinate $(C_8H_{12})Ir^+$ units. Reaction of compound **1** with $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ and CH_3COOH in CH_3CN yields $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_5$ (**3**) [$a = 16.618$ (4) Å, $b = 16.548$ (4) Å, $c = 30.729$ (6) Å, $\alpha = 87.02$ (2)°, $\beta = 94.57$ (2)°, $\gamma = 114.20$ (2)°, triclinic; $P\bar{1}\text{-}C_i^1$; $Z = 2$]. According to single-crystal diffraction and ^{17}O NMR spectroscopic studies, the anion of **3** contains two $Nb_2W_4O_{19}^{4-}$ ions linked together in an edge-to-edge fashion by two four-coordinate $(C_8H_{12})Ir^+$ units and one proton. The trimetaphosphate complex $[(C_8H_{12})Ir(P_3O_9)][(n\text{-}C_4H_9)_4N]_2$ **4** [$a = 11.324$ (2) Å, $b = 13.288$ (2) Å, $c = 34.035$ (5) Å, $\beta = 101.24$ (1)°, monoclinic; $P2_1/c\text{-}C_{2h}^5$; $Z = 4$] is prepared from $[(C_8H_{12})Ir(NCCH_3)_2]PF_6$ and $P_3O_9[(n\text{-}C_4H_9)_4N]_3$. A single-crystal X-ray diffraction study of compound **4** revealed the presence of discrete $[(C_8H_{12})Ir(P_3O_9)]^{2-}$ anions in which the iridium center is square-pyramidally coordinated, with the two cyclooctadiene olefinic units occupying basal sites and three trimetaphosphate oxygens spanning the remaining basal and apical sites. Addition of 250 equiv of CD_3CN/equiv of Ir to CD_3NO_2 solutions of **1**, **3**, and **4**, all 3.5 mM in Ir, completely decomposes the anion of **1**, partially decomposes the anion of **3**, but leaves the anion of **4** intact, according to ^1H NMR spectroscopic data.

Organorhodium(I) and organoiridium(I) complexes are known to have an extensive reaction chemistry in fluid solution and on solid oxide supports.[1] In order to combine key features associated with solution and solid-state environments, reactions of these complexes with both main-group and transition-metal polyoxoanions have been investigated.[2–5] Two polyoxoanion-supported

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[†] Crystalytics Co. and University of Nebraska.
[‡] University of Illinois.

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