

Synthesis and characterisation of ruthenium carbonyl complexes with cyclometallated ligands derived from senecialdimine

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Abstract

From thermal reactions of $\text{Ru}_2(\text{CO})_{12}$ with senecialdimine, $(\text{CH}_3)_2\text{C}=\text{CHCH}=\text{NR}$ ($\text{R} = \text{iPr}$ (**a**), t-Bu (**b**)), in refluxing heptanes the following complexes have been isolated and characterised: $\text{Ru}_2(\text{CO})_6[(\text{CH}_3)_2\text{C}(\text{H})\text{CC}(\text{H})\text{NR}]$ (**2a,b**), $\text{Ru}_2(\text{CO})_6[\text{C}(\text{H})\text{C}(\text{CH}_3)_2\text{C}(\text{H})\text{C}(\text{H})=\text{NR}]$ (**3a,b**), $[\text{HRu}_6(\text{CO})_{18}]_2\text{-}[\text{C}(\text{H})=\text{C}(\text{CH}_3)_2\text{-}4\text{-CH}_3\text{-C}_3\text{H}_3\text{N}]$ (**4a**), $\text{HRu}_6(\text{CO})_{18}[(\text{CH}_3)_2\text{C}(\text{H})\text{CH}_2\text{C}=\text{NR}]$ (**5a**), and $\text{Ru}_2(\text{CO})_6[\text{C}(\text{H})\text{C}(\text{CH}_3)_2\text{C}(\text{H})\text{C}=\text{N}(\text{HR})]$ (**6b**). The complexes **3a**, **4a**, and **6b** have been characterised by X-ray structure determinations. Crystals of **3a** are monoclinic, space group $P2_1/n$, with $a = 11.217(4)$ Å, $b = 10.991(2)$ Å, $c = 14.214(3)$ Å, $\beta = 94.38(2)^\circ$, $Z = 4$ and $R = 0.0264$. Crystals of **4a** are monoclinic, space group $P2_1/n$, with $a = 10.483(2)$ Å, $b = 15.910(3)$ Å, $c = 24.995(5)$ Å, $\beta = 101.56(2)^\circ$, $Z = 4$ and $R = 0.0279$. Crystals of **6b** are monoclinic, space group $P2_1/n$, with $a = 11.449(2)$ Å, $b = 12.012(2)$ Å, $c = 13.561(3)$ Å, $\beta = 102.69(2)^\circ$, $Z = 4$ and $R = 0.0239$. The other complexes were characterised spectroscopically. Complex **6b** contains a novel η^3 -coordinated metallocyclopentadiene fragment, the second of its kind reported so far. The anomalous η^3 -coordination is attributed to the presence of an amino substituent on one of the metallated carbon atoms causing redistribution of electrons over the ligand skeleton. Possible formation pathways of the complexes are described.

Keywords: Ruthenium; Carbonyl complexes; Cyclometallated ligands; Imine; X-ray diffraction; Cluster

1. Introduction

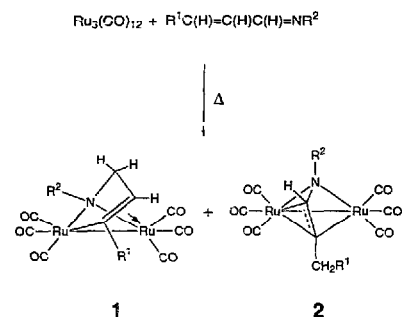
In the course of our study on the reactivity of ruthenium carbonyl complexes with monoazadienes some interesting cyclometallated ligand types have been obtained [1–3]. The first two isolable complexes from thermal reactions of $\text{Ru}_2(\text{CO})_{12}$ and monoazadienes (MADs) of type $\text{R}'\text{C}(\text{H})=\text{C}(\text{H})\text{C}(\text{H})=\text{NR}$ are the dinuclear complexes $\text{Ru}_2(\text{CO})_6[\text{R}'\text{C}=\text{C}(\text{H})\text{CH}_2\text{NR}]$ (**1**) and $\text{Ru}_2(\text{CO})_6[\text{R}'\text{CH}_2\text{CC}(\text{H})\text{NR}]$ (**2**) (see Scheme 1), both of which contain a cyclometallated isomerised MAD ligand that bridges the intermetallic bond. Complex **2** is usually obtained as the minor product (10–40%). To enable a more extensive study towards the reactivity of

2, which exhibits dynamical behaviour in solution [3] and interesting photochemical reactivity [4], improving its yield was an important goal. It was anticipated that substitution of H_β by a methyl group¹ would block the reaction path leading to **1** and hence **2** would become the major product. Furthermore, cyclometallation of the MAD ligand at other positions might become kinetically feasible, possibly leading to new types of ligand.

In this paper we report on the products emerging from thermal reactions of ruthenium dodecacarbonyl and senecialdimine (R-SAI; $(\text{CH}_3)_2\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{NR}$, $\text{R} = \text{iPr}$, t-Bu). One of the new organometallic complexes obtained contains a novel $\mu_2\text{-}\eta^3$ -allyl-amino-

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¹ Suffixes to the atoms refer to: $[\text{R}(\text{CH}_3)_2]_n$, $[\text{C}]_m = [\text{CH}]_n$, $[\text{CH}]_m = \text{NR}$.



Scheme 1. Products formed during thermal reactions of $\text{Ru}_3(\text{CO})_{12}$ with crotonaldimine.

carbene ligand, the second of its kind reported thus far. In another reaction product a remarkable coupling of two senecioldimines into a trisubstituted pyridinium moiety has taken place.

2. Experimental section

2.1. Materials and apparatus

^1H and ^{13}C NMR data were obtained on Bruker AC100 and WM250 spectrometers. IR spectra were recorded with Perkin–Elmer 283 and Nicolet 7199 B spectrophotometers using NaCl solution cells of 0.5 mm path length. Field desorption (FD) mass spectra [5] were obtained with a Varian MAT-77 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 90 °C.

The HPLC separations were performed with a modular Gilson liquid chromatographic system consisting of two 303 elution pumps, an 811 mixing chamber, a 7125 Rheodyne injector equipped with a 20 ml (analytical) or 2 ml (preparative) sample loop an 802c manometric module, and an 111 B UV detector operated at 254 nm, all obtained from Meyvis, Netherlands. The system was controlled by an Apple Macintosh SE with Rainin software. Reversed phase columns: Hypersil ODS 5-mm (100 \times 4.8 mm; analytical and 250 \times 9.4 mm; semi-preparative).

Solvents were carefully dried and distilled prior to use. All preparations were carried out under an atmosphere of dry nitrogen using Schlenk techniques. Silica gel for column chromatography (kieselgel 60, 70–230 mesh, Merck, Darmstadt, Germany) was dried before

use. $\text{Ru}_3(\text{CO})_{12}$ was used as-purchased from Strem Chemicals Inc. (USA).

The monoazadienes *N*-isopropyl-senecioldimine (iPr-SAI) and *N*-*tert*-butyl-senecioldimine (t-Bu-SAI) were prepared by condensation of senecioldialdehyde with the relevant amine according to standard procedures [6,7]. The senecioldimines were distilled at 0.1 mmHg and were stored under an atmosphere of nitrogen at –80 °C. ^1H NMR for $(\text{CH}_3)_2\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{N}$ -iPr (CDCl_3 , 100.1 MHz, 298 K, δ ppm): 8.16 (d, 9.5 Hz, C(H)=N), 5.94 (m, C=C(H)), 3.30 (sept, 6.5 Hz, N(C(H)C(H) $_2$)), 1.88, 1.83 (m, m, (C(H) $_2$ C=C(H))), 1.15 (d, 6.5 Hz, N C(H)(C(H) $_3$) $_2$). ^{13}C NMR for $(\text{CH}_3)_2\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{N}$ -iPr (CDCl_3 , 25.2 MHz, 298 K): 156.8 (C(H)=N); 145.9 ((CH $_3$) $_2$ C=C); 125.8 ((CH $_3$) $_2$ C=C); 61.4 (NC(H)(CH $_3$) $_2$); 26.5, 18.6 ((CH $_3$) $_2$ C=C); 24.3 (NC(H)(CH $_3$) $_2$).

^1H NMR for $(\text{CH}_3)_2\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{N}$ -t-Bu (CDCl_3 , 100.1 MHz, 298 K, δ ppm): 8.17 (d, 9.0 Hz, C(H)=N), 5.94 (m, C=C(H)), 1.85, 1.79 (m, m, (C(H) $_2$ C=C(H))), 1.14 (s, NC(C(H) $_3$) $_3$). ^{13}C NMR for $(\text{CH}_3)_2\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{N}$ -t-Bu (CDCl_3 , 25.2 MHz, 298 K): 153.7 (C(H)=N); 145.0 ((CH $_3$) $_2$ C=C); 128.1 (CH $_3$) $_2$ C=C); 56.6 (NC(C(H) $_3$) $_3$); 29.7 (NC(CH $_3$) $_3$); 16.3, 18.4 ((C(H) $_3$) $_2$ C=C).

2.2. Synthesis of $\text{Ru}_3(\text{CO})_6[(\text{CH}_3)_2\text{C}(\text{H})\text{C}(\text{H})\text{NR}]$ (R = iPr (2a), t-Bu (2b))

A solution of $\text{Ru}_3(\text{CO})_{12}$ (0.64 g; 1 mmol) and R-SAI (R = iPr, t-Bu; 3 mmol) in 50 ml of heptanes was stirred at 100 °C for 24 h. After this period the solvent was evaporated under vacuum and the residue was fractionated on silica. Elution with hexane afforded a pale yellow fraction of $\text{Ru}_3(\text{CO})_6[(\text{CH}_3)_2\text{C}(\text{H})\text{C}(\text{H})\text{NR}]$ (R = iPr (2a), t-Bu (2b)) in a yield of about 60%.

Data for 2a. ^1H NMR (CDCl_3 , 100.1 MHz, 298 K): 6.89 (s, CC(H)N), 2.59, 2.40 (2 \times sept, 6.5 Hz, NC(H)(CH $_3$) $_2$, CC(H)(CH $_3$) $_2$), 1.09, 0.90 (2 \times d, 6.5 Hz, NC(H)(CH $_3$) $_2$, CC(H)(CH $_3$) $_2$); ^{13}C NMR (CDCl_3 , 62.9 MHz, 263 K): 197.1 (6 \times CO), 148.2 (CC(H)N), 107.1 (CC(H)N), 56.1 (NC(H)(CH $_3$) $_2$), 35.3 (C(C(H)CH $_3$) $_2$), 25.7, 25.1 (NC(H)(CH $_3$) $_2$, CC(H)(CH $_3$) $_2$); IR ($\nu(\text{CO})$ cm^{-1} , hexane solution): 2075 (m), 2043 (vs), 2003 (s), 1991 (s), 1979 (m). Anal. Found (calcd) for $\text{Ru}_2\text{C}_{12}\text{H}_{13}\text{NO}_6$ (2a): C, 33.99 (33.94); H, 3.14 (3.05); N, 2.99 (2.83); FD/MS: m/e 495 (495).

Data for 2b. ^1H NMR (CDCl_3 , 100.1 MHz, 298 K): 6.92 (s, CC(H)N), 2.59 (sept, 6.5 Hz, CC(H)(CH $_3$) $_2$), 1.09 (d, 6.5 Hz, CC(H)(CH $_3$) $_2$), 0.90 (s, NC(C(H) $_3$) $_3$); ^{13}C NMR (CDCl_3 , 25.2 MHz, 263 K): 197.6 (6 \times CO), 146.2 (CC(H)N), 106.1 (CC(H)N), 55.6 (NC(C(H) $_3$) $_3$), 35.7 (C(C(H)CH $_3$) $_2$), 30.5 (NC(C(H) $_3$) $_3$), 25.4 (CC(H)(CH $_3$) $_2$); IR ($\nu(\text{CO})$ cm^{-1} , hexane solution):

2074 (m), 2041 (vs), 2002 (s), 1989 (s), 1978 (m). Anal. Found (calcd) for $Ru_2C_{15}H_{17}NO_6$ (**2b**): C, 35.49 (35.36); H, 3.37 (3.37); N, 2.73 (2.75); FD-MS: *m/e* 509 (509).

2.3. Synthesis of $Ru_2(CO)_6[(CH)C(CH_3)C(H)C(H)N-iPr]$ (**3a**)

A solution of $Ru_3(CO)_{12}$ (0.64 g; 1 mmol) and *iPr*-SAI (3 mmol) in 50 ml of heptanes was stirred at reflux (oil bath temperature 120°C) for 72 h. After this period the reaction mixture was filtered over a short column (3 cm) of silica and the filtrate was evaporated to dryness. The residue was chromatographed on silica. Elution with hexane afforded a pale yellow band of **2a** (45%). Subsequent elution with hexane–diethyl ether (9:1) gave a second yellow band which contained $Ru_2(CO)_6[(CH)C(CH_3)C(H)C(H)N-iPr]$ (**3a**) in a yield of about 20%. Yellow crystals of **3a** suitable for X-ray diffraction analysis were obtained by cooling a concentrated solution of **3a** in hexane at –90°C.

Data for **3a**. 1H NMR ($CDCl_3$, 298 K): 8.49 (d, 2.3 Hz, C(H)C(CH₃)C), 7.99 (d, 5.5 Hz, N=C(H)), 3.45 (sept, 6.5 Hz, NC(H)C(H)₂), 3.30 (dd, 5.5 Hz, 2.3 Hz, C(H)C(H)=N), 2.47 (s, C(H)C(CH₃)C(H)) 1.07, 0.90 (d, 6.5 Hz, NC(H)C(H)₂); ^{13}C NMR ($CDCl_3$, 263 K): 202.1, 198.3, 192.5 (3 × CO), 173.8 (N=C(H)), 144.7 (C(H)C(CH₃)C(H)), 104.6 (C(H)C(CH₃)C(H)), 64.3 (N=C(H)C(H)₂), 51.3 (C(H)C(H)=N), 29.9 (C(H)C(CH₃)C(H)), 22.9, 22.0 (NC(H)C(H)₂); IR ($\nu(CO)$ cm^{-1} , hexane solution): 2072 (s), 2031 (vs), 2001 (vs), 1988 (s), 1973 (m), ($\nu(C-N)$), KBr: 1631 cm^{-1} . Anal. Found (calcd) for $Ru_2C_{11}H_{13}NO_6$ (**3a**): C, 34.18 (34.08); H, 2.70 (2.66); N, 2.82 (2.84); FD-MS: *m/e* 493 (493).

2.4. Synthesis of $[HRu_6(CO)_{18}]^- [2-[C(H)=C(CH_3)_2]-4-CH_3-C_3H_3N]^+$ (**4a**)

A solution of $Ru_3(CO)_{12}$ (0.64 g; 1.0 mmol) and *iPr*-SAI (0.27 g; 2 mmol) in 50 ml of heptanes was stirred at reflux for 20 h. After removal of the solvent under vacuum, the residue was chromatographed on silica. Elution with diethyl ether gave an orange band containing a mixture of compounds including **2a** and **3a**. Subsequent elution with dichloromethane afforded a red-brown band of $[HRu_6(CO)_{18}]^- [2-[C(H)=C(CH_3)_2]-4-CH_3-C_3H_3N]^+$ (**4a**) in a yield of 20 mg (3%). Dark brown crystals of **4a** suitable for X-ray diffraction analysis were obtained by cooling a saturated solution of **4a** in dichloromethane–diethyl ether at –90°C.

Data for **4a**. 1H NMR (CD_2Cl_2 , 250.1 MHz, 297 K): 16.46 (s, hydride), 8.33 (d, 6.0 Hz), 7.69 (d, 6.0 Hz), 7.55 (s), 6.26 (s), 5.10 (sept, 6.0 Hz, NC(H)C(H)₂), 2.67 (s), 2.12 (d, 1.2 Hz), 1.87 (d, 1.2 Hz), 1.61 (d,

6.0 Hz, NC(H)C(H)₂); IR (dichloromethane, $\nu(CO)$ cm^{-1}): 2022 (s), 1956 (vw) (lit.: 2020 (s), 1953 (vw) [8]). Anal. Found (calcd) for $Ru_6C_{31}H_{21}NO_{18}$ (**4a**): C, 28.92 (28.60); H, 1.77 (1.63); N, 1.06 (1.08); FD-MS: *m/e* 190 (190).

2.5. Synthesis of $Ru_2(CO)_6[(CH)C(CH_3)C(H)C(H)N-t-Bu]$ (**3b**) and $Ru_2(CO)_6[(CH)C(CH_3)C(H)C(H)N-t-Bu]$ (**6b**)

A solution of $Ru_3(CO)_{12}$ (0.64 g; 1 mmol) and *t-Bu*-SAI (3 mmol) in 50 ml of heptanes was stirred at reflux for 24 h. After this period the solvent was removed under vacuum and the red-brown residue chromatographed on silica. Elution with hexane gave a pale yellow band of **2b** (0.22 g; 40%). Subsequent elution with hexane–diethyl ether (2:1) gave a yellow band of $Ru_2(CO)_6[(CH)C(CH_3)C(H)C(H)N-t-Bu]$ (**3b**) and $Ru_2(CO)_6[(CH)C(CH_3)C(H)C(H)N-t-Bu]$ (**6b**) in a total yield of 0.36 g (ratio **3b**:**6b** was about 1:2). Separation of **3b** and **6b** could be achieved by preparative HPLC on a reversed phase column. To this end a mixture of **3b** and **6b** (0.05 g/run) was dissolved in a minimum amount of dichloromethane and passed through a semi-preparative RP-HPLC column using an isocratic mixture of methanol–water (87:13) as the mobile phase at a flow rate of 2 ml min⁻¹. Two fractions were collected (first fraction (**6b**): 27–30 ml; second fraction (**3b**): 32.5–35.5 ml). After a total of 22 runs the solvent of the pooled fractions was removed under vacuum affording **3b** and **6b** as spectroscopically and analytically pure compounds. Yellow crystals of **6b** suitable for X-ray diffraction analysis were obtained by cooling a concentrated solution of **6b** in hexane at –90°C.

Data for **3b**. 1H NMR ($CDCl_3$, 100.1 MHz, 298 K): 8.48 (d, 2.5 Hz, C(H)C(CH₃)C), 8.21 (d, 6.0 Hz, N=C(H)), 3.32 (dd, 6.0 Hz, 2.5 Hz, C(H)C(H)=N), 2.46 (s, C(H)C(CH₃)C(H)) 1.08 (s, NC(H)₂); ^{13}C NMR ($CDCl_3$, 25.2 MHz, 263 K): 176.3 (N=C(H)), 145.3 (C(H)C(CH₃)C(H)), 104.4 (C(H)C(CH₃)C(H)), 61.8 (NC(CH₃)₂), 51.0 (C(H)C(H)=N), 31.7 (NC(CH₃)₂), 29.9 (C(H)C(CH₃)C(H)); IR ($\nu(CO)$ cm^{-1} , hexane solution): 2073 (m), 2031 (vs), 1999 (s), 1987 (m), 1973 (w). Anal. Found (calcd) for $Ru_2C_{15}H_{15}NO_6$ (**3b**): C, 35.24 (35.51); H, 2.91 (2.98); N, 2.67 (2.76); FD-MS: *m/e* 507 (507).

Data for **6b**. 1H NMR ($CDCl_3$, 100.1 MHz, 298 K): 6.71 (d, 2.5 Hz, C(H)=C(CH₃)), 5.57 (N(H)), 4.91 (d, 2.5 Hz, C(H)=CN), 2.31 (s, C(H)=C(CH₃)) 1.35 (s, NC(CH₃)₂); ^{13}C NMR ($CDCl_3$, 62.9, 248 K): 211.3 (C(H)=C(NH)), 200.5, 199.8, 195.9 (3 × CO), 197.6 (3 × CO), 135.0 (C(H)=C(CH₃)), 124.6 (C(H)=C(CH₃)), 69.7 (C(CH₃)C(H)=C), 55.5 (N=C(H)₂), 29.0 (NC(CH₃)₂), 23.0 (C(H)=C(CH₃)); IR ($\nu(CO)$ cm^{-1} , hexane solution): 2071 (m), 2038 (s), 2001 (s), 1989 (s), 1984 (w), 1966

(m); IR ($\nu(\text{NH}) \text{ cm}^{-1}$, KBr): 3420. Anal. Found (calcd) for $\text{Ru}_2\text{C}_{15}\text{H}_{15}\text{NO}_6$ (**6b**): C, 35.46 (35.51); H, 3.04 (2.98); N, 2.70 (2.76); FD-MS: m/e 507 (507).

2.6. Structure determination and refinement of **3a**, **4a** and **6b**

Crystal data and numerical details of the structure determinations are given in Table 1. Crystals of the three compounds were glued on glass-fibres and transferred to an Enraf–Nonius CAD-4 diffractometer for data collection at either room temperature (**3a** and **4a**) or at 100 K (**6b**). Unit cell parameters were determined from a least squares treatment of SET4 setting angles and were checked for the presence of higher lattice symmetry [9]. All data were collected in ω - 2θ scan mode, data were corrected for Lp and for the observed linear decay of the intensity control reflections; redundant data were merged into a unique dataset. Absorption correction was applied using the DIFABS [10] method. The

structures were solved with direct methods (SHELXS86 [11]) followed by subsequent difference Fourier syntheses. Refinement on F^2 using all unique reflections was carried out by full matrix least squares techniques.

The hydride atom of **4a** and the (N,C)-H atoms of **3a** and **6b** were located from difference Fourier maps and included in the refinement with free positional and isotropic thermal parameters. Other H-atoms of the three complexes were introduced on calculated positions and included in the refinement riding on their carrier atoms with isotropic thermal parameters related to the U_{eq} of the carrier atoms. All non-H atoms were refined with anisotropic thermal parameters. Weights were introduced in the final refinement cycles.

Neutral atom scattering factors and anomalous dispersion factors were taken from Ref. [12]. All calculations were performed with SHELXL93 [13] and the PLATON package [14] (geometrical calculations and illustrations) on a DEC-5000 cluster.

Table 1
Crystal data and details of the structure determination

	3a	4a	6b
<i>Crystal data</i>			
Formula	$\text{C}_{15}\text{H}_{15}\text{NO}_6\text{Ru}_2$	$\text{HRu}_2(\text{CO})_4 \cdot \text{C}_{15}\text{H}_{20}\text{N}$	$\text{C}_{15}\text{H}_{15}\text{NO}_6\text{Ru}_2$
Mol. wt.	493.40	1301.92	507.43
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (Nr. 14)	$P2_1/n$ (Nr. 14)	$P2_1/n$ (Nr. 14)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.214(4), 10.991(2), 14.214(3)	10.483(2), 15.910(3), 24.995(5)	11.499(2), 12.012(2), 13.561(3)
β (deg)	94.38(2)	101.56(2)	102.69(2)
<i>V</i> (Å ³)	1747.3(8)	4084(1)	1827.4(6)
<i>Z</i>	4	4	4
D_{calc} (g cm ⁻³)	1.876	2.117	1.844
<i>F</i> (000)	960	2488	992
μ (cm ⁻¹)	17.5	22.3	16.8
Crystal size (mm ³), colour	0.45 × 0.39 × 0.14, yellow	0.08 × 0.18 × 0.30, dark-brown	0.12 × 0.15 × 0.33, yellowish
<i>Data collection</i>			
Temperature (K)	298	298	100
θ_{min} , θ_{max}	1.44, 25.00	0.83, 23.00	1.54, 27.50
Radiation	Mo K α (Zr-filtered), 0.71073 Å	Mo K α (Zr-filtered), 0.71073 Å	Mo K α (graphite monochromated), 0.71073 Å
$\Delta\omega$ (deg)	0.80 : 0.35 tan θ	0.40 + 0.35 tan θ	0.85 + 0.35 tan θ
Hor. and vert. aperture (mm)	3.00, 4.0	3.00, 3.00	4.00, 4.50
X-ray exposure time (h)	141	113	125
Linear decay (%)	0.0	0.0	1.5
Reference reflections	200, 002	200, 020, 00-4	21-3, 2-1-3, -12-2
Data set	<i>h</i> -13:13; <i>k</i> -13:0; <i>l</i> -16:16	<i>h</i> -11:11; <i>k</i> 0:17; <i>l</i> -27:0	<i>h</i> -18:15; <i>k</i> -19:19; <i>l</i> -21:14
Total data	6499	6075	8402
Total unique data	3073 ($R_i = 0.0287$)	5668	4201 ($R_i = 0.0385$)
Observed data	3073	5660 ($F_o^2 > -3\sigma(F_o^2)$)	4199
DIFABS correction range	0.716–1.182	0.780–1.329	0.736–1.593
<i>Refinement</i>			
No. of refl. and params.	3073, 227	5660, 514	4199, 233
Weighting scheme	$w = 1.0/[\sigma^2(F_o^2) + (0.0370P)^2 + 0.60P]$	$w = 1.0/[\sigma^2(F_o^2) + (0.0285P)^2 + 3.68P]$	$w = 1.0/[\sigma^2(F_o^2) + (0.0280P)^2 + 0.42P]$
Final R_1 , wR_2 , S	0.0264, 0.0691, 1.037	0.0279, 0.0659, 1.073	0.0239, 0.0509, 1.028
$f(\Delta/\sigma)_n$ and max. in final cycle	0.0006, 0.001	0.00, 0.003	0.000, 0.001
Min. and max. resd. dens. (e ⁻ Å ⁻³)	-0.52, 0.77	-0.42, 0.52	-0.80, 0.80

3. Results and discussion

3.1. Formation of the complexes

The formation of products resulting from reactions between $\text{Ru}_3(\text{CO})_9$ and senealdimine, $(\text{CH}_3)_2\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{NR}$ (R-SAI; R = *i*Pr, *t*-Bu), depends on the reaction temperature and the R-substituent.

The reaction of $\text{Ru}_3(\text{CO})_9$ with *i*Pr-SAI at 80–100 °C in heptane solution results in the formation of $\text{Ru}_2(\text{CO})_6[(\text{CH}_3)_2\text{C}(\text{H})\text{C}(\text{H})\text{N-}i\text{Pr}]$ (**2a**) as the major product (ca. 60%) and a variety of by-products in small amounts (< 5%). When this reaction is performed in refluxing heptane, compound **2a** is still the major product, but some of the by-products are formed in larger amounts. Of these the yellow compound $\text{Ru}_2(\text{CO})_6[\text{C}(\text{H})\text{C}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{H})=\text{N-}i\text{Pr}]$ (**3a**), which contains a double metallated and dehydrogenated (–2H) *i*Pr-SAI ligand, and the red-brown ionic complex $[\text{HRu}_6(\text{CO})_{18}]^{+}[2\text{-}(\text{C}(\text{H})=\text{C}(\text{H})_2)_2\text{-}4\text{-CH}_3\text{-C}_4\text{H}_3\text{N-}i\text{Pr}]^{-}$ (**4a**) could be purified and isolated by column chromatography. The presence of the H_2 adduct $\text{HRu}_2(\text{CO})_6[(\text{CH}_3)_2\text{C}(\text{H})\text{C}(\text{H})\text{C}=\text{N-}i\text{Pr}]$ (**5a**) in the reaction mixture could be established spectroscopically as well, but all attempts to purify this compound have failed thus far.²

The thermal reaction of $\text{Ru}_3(\text{CO})_9$ with *t*-Bu-SAI proceeds considerably slower and gives $\text{Ru}_2(\text{CO})_6[(\text{CH}_3)_2\text{C}(\text{H})\text{C}(\text{H})\text{N-}t\text{-Bu}]$ (**2b**), $\text{Ru}_2(\text{CO})_6[\text{C}(\text{H})\text{C}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{H})=\text{N-}t\text{-Bu}]$ (**3b**), and $\text{Ru}_2(\text{CO})_6[\text{C}(\text{H})\text{C}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{H})\text{N-}t\text{-Bu}]$ (**6b**) as the major products, whereas less by-products are formed compared to the reaction with *i*Pr-SAI. The yield of **3b** and **6b** increases with the reaction temperature (see Section 2). Compound **3b** can thermally not be converted into the isomeric compound **6b** or vice versa. An overview of these reactions is presented in Scheme 2. The complexes **3a**, **4a** and **6b** have been characterised crystallographically. The complexes **2a**, **3b**, and **5a** have been characterised on the basis of their analytical and spectroscopic data (see Section 2).

3.2. Structural and spectroscopic characteristics of the complexes

The ^1H and ^{13}C NMR spectra of **2a** and **2b** show that these complexes are fluxional in solution, just as their structural analogues $\text{Ru}_2(\text{CO})_6[\text{RCH}_2\text{C}(\text{H})\text{NR}]$ of

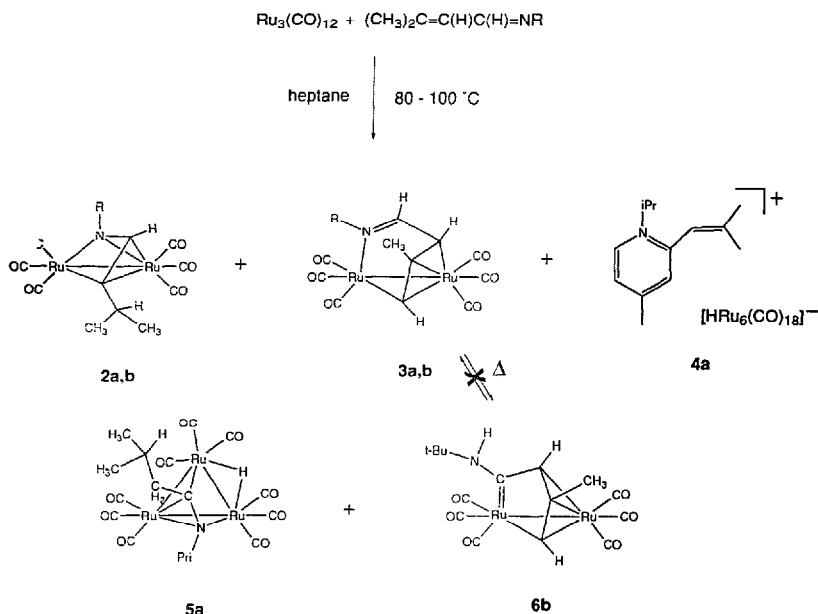
which an X-ray structure has been determined for R = CH_3 , R' = *t*-Bu [15]. For example, at 298 K the *i*Pr methyl protons of **2a** and **2b** lack diastereotopicity and at 263 K the six CO ligands give rise to single sharp resonances in the ^{13}C NMR spectra. The fluxional process for **2** involves a 'windshield wiper' process of the azaallyl ligand in combination with local scrambling of the CO ligands [16].

The molecular geometry of **3a** along with the adopted numbering scheme are shown in Fig. 1. Selected bond lengths and bond angles are given in Table 2. The organometallic compound **3a** consists of a 'saw-horse'-type $\text{Ru}_2(\text{CO})_6$ -core and a formally $6e^-$ -donating $\sigma\text{-N}, \mu_2\text{-}\eta^3$ -allyl-imine ligand which bridges the single Ru–Ru bond of 2.7773(11) Å. The metal carbonyl part exhibits normal structural features. The Ru–C(O) distances fall within the region of 1.88–1.92 Å, except the rather long Ru(1)–C(2) distance of 1.964(4) Å. The elongation of the latter can readily be ascribed to the *trans*-influence exerted by the carbon atom C(10). The cyclometallated *i*Pr-SAI ligand is part of a six-membered azaruthenacycle and coordinated to Ru(1) via a $\sigma\text{-N}$ bond and a $\sigma\text{-C}(10)$ bond and η^3 -coordinated to Ru(2) via the C(8)–C(9)–C(10) moiety. The Ru(1)–N bond length of 2.115(3) Å is indicative for a normal dative bond and the imine N–C(7) bond length of 1.275(5) Å points to a localized double bond. The carbon atom C(10) is σ -coordinated to Ru(1), the bond distance of 2.072(4) Å being slightly shorter than for normal Ru–C bonds [17]. The Ru–C distances of the Ru(2)-allyl unit are nearly equal (2.210(4)–2.218(4) Å). The C–C distances within the allyl unit, however, differ significantly; the C(8)–C(9) and C(9)–C(10) distances amount to 1.439(6) and 1.381(6) Å respectively. The rather short C(7)–C(8) distance of 1.442(6) Å indicates effective electron delocalisation between the unsaturated imine and allyl fragments. This delocalisation might be the cause for the asymmetry in the allyl fragment. The $\sigma\text{-N}, \mu_2\text{-}\eta^3$ -allyl-imine ligand and its coordination to the dinuclear metal core in **3** closely resembles that encountered³ in $\text{Fe}_2(\text{CO})_6[\text{C}(\text{OCH}_3)\text{C}(\text{H})\text{C}(\text{H})\text{C}(\text{OCH}_3)=\text{NR}]$ [10].

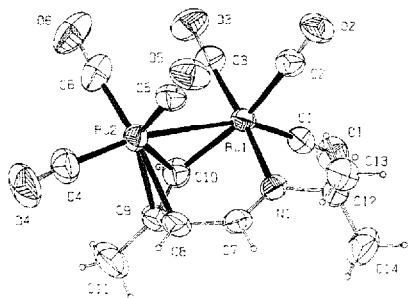
The ^1H NMR resonances of **3a** and **3b** could readily be assigned on the basis of their chemical shifts and coupling patterns. On the basis of a $^1\text{H}, ^{13}\text{C}$ -COSY spectrum for **3a**, the ^{13}C NMR resonances could be attributed as well. Both the ^1H and ^{13}C NMR data are in agreement with the molecular structure of **3a** in the solid state.

The molecular structure of **4a** is shown in Fig. 2. Selected bond lengths and angles are given in Table 3. The molecular structure of **4a** contains two residues, clearly revealing its ionic character. It consists of an anionic inorganic part, the well known $[\text{HRu}_6(\text{CO})_{18}]^{-}$ cluster and a cationic organic part, a trisubstituted pyridinium ion. In analogy with the reported structure of

² Data for **5a**. ^1H NMR (CDCl_3 , 250.1 MHz, 297 K): 4.04 (sept, 6.5 Hz, $\text{N}(\text{H})\text{C}(\text{H})_2$), 2.67 (d, 7.0 Hz, $\text{N}=\text{CCH}_2$), 2.10 (tsept, 7.0, 6.5, $\text{CH}_2\text{C}(\text{H})\text{C}(\text{H})_2$), 1.09 (d, 6.5 Hz, $\text{CCH}_2\text{C}(\text{H})_2$), 0.99 (d, 6.5 Hz, $\text{N}(\text{H})\text{C}(\text{H})_2$), –17.84 (s, hydride); IR (hexane, $\nu(\text{CO})$ cm^{-1}): 2089 (w), 2065 (s), 2043 (w), 2034 (vs), 2019 (s), 2002 (m), 1994 (w), 1977 (w), 1974 (w, br); FD-MS: m/e 682 (682).

Scheme 2. Overview of the products formed during thermal reactions of $\text{Ru}_3(\text{CO})_{12}$ with senecioldimine.

this $[\text{HRu}_6(\text{CO})_{18}]^+$ cluster, the current Ru_6 -core has two equivalent faces that are approximately equilateral (mean $\text{Ru}-\text{Ru}$, 2.874(16) Å (lit.: 2.877(13) Å) [8]). These are slightly twisted from O_h symmetry so the remaining bond lengths are alternately long (mean $\text{Ru}-\text{Ru}$,

Fig. 1. Thermal ellipsoid plot of **3a** drawn at the 40% probability level, with the adopted numbering scheme.Table 2
Selected bond distances (Å) and bond angles (deg) of **3a**

Ru(1)–Ru(2)	2.7773(11)	Ru(2)–C(8)	2.217(4)
Ru(1)–N(1)	2.115(3)	Ru(2)–C(9)	2.210(4)
Ru(1)–C(1)	1.917(4)	Ru(2)–C(10)	2.218(4)
Ru(1)–C(2)	1.964(4)	N(1)–C(7)	1.275(5)
Ru(1)–C(3)	1.887(4)	N(1)–C(12)	1.493(5)
Ru(1)–C(10)	2.072(4)	C(7)–C(8)	1.442(6)
Ru(2)–C(4)	1.907(6)	C(8)–C(9)	1.439(6)
Ru(2)–C(5)	1.900(4)	C(9)–C(10)	1.381(6)
Ru(2)–C(6)	1.908(5)	C(9)–C(11)	1.524(6)
Ru(2)–Ru(1)–C(1)	150.05(13)	Ru(1)–N(1)–C(12)	121.6(2)
Ru(2)–Ru(1)–C(10)	51.99(10)	C(7)–N(1)–C(12)	118.2(3)
Ru(2)–Ru(1)–N(1)	85.03(9)	N(1)–C(7)–C(8)	124.9(4)
C(3)–Ru(1)–N(1)	174.90(16)	Ru(2)–C(8)–C(9)	70.8(2)
C(2)–Ru(1)–C(10)	164.00(14)	Ru(2)–C(8)–C(7)	112.2(3)
Ru(1)–Ru(2)–C(4)	168.74(16)	Ru(2)–C(9)–C(10)	72.1(2)
Ru(1)–Ru(2)–C(5)	82.42(13)	Ru(2)–C(9)–C(18)	71.3(2)
Ru(1)–Ru(2)–C(6)	96.72(16)	Ru(2)–C(9)–C(11)	125.9(3)
Ru(1)–Ru(2)–C(8)	79.66(11)	C(8)–C(9)–C(10)	117.5(4)
Ru(1)–Ru(2)–C(9)	74.69(11)	C(8)–C(9)–C(11)	119.0(4)
Ru(1)–Ru(2)–C(10)	47.40(11)	C(10)–C(9)–C(11)	123.4(4)
C(5)–Ru(2)–C(10)	128.86(18)	N(1)–C(7)–C(8)	124.9(4)
C(6)–Ru(2)–C(8)	162.16(18)	Ru(2)–C(10)–Ru(1)	80.61(12)
Ru(1)–N(1)–C(7)	119.9(3)	Ru(2)–C(10)–C(9)	71.5(2)

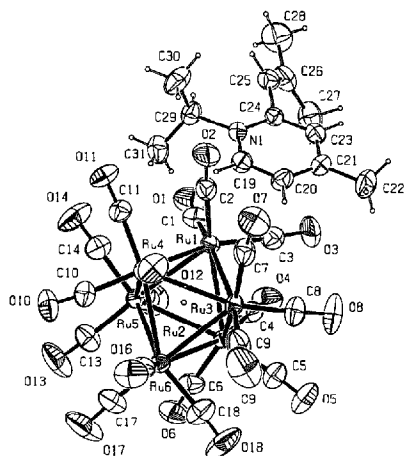


Fig. 2. Thermal ellipsoid plot of **4a** drawn at the 40% probability level, with the adopted numbering scheme.

2.93(2) Å (lit.: 2.924(3) Å) and short (mean Ru–Ru, 2.844(7) Å (lit.: 2.839(6) Å)). The bond lengths within the organic part of the molecule indicate extensive electron delocalisation within the pyridinium ring. There is little or no conjugation of the pyridinium ring with the 2-methyl-1-propen-1-yl substituent as is indicated by the single C(24)–C(25) bond of 1.478(8) Å and the dihedral angle of about 50° between these two unsaturated fragments.

The ^1H NMR resonance for the interstitial hydride of the $[\text{HRu}_6(\text{CO})_9]^-$ unit of **4a** is found at 16.46 ppm, in line with its unusual environment and in agreement with the literature [8]. The remaining ^1H NMR signals could all be assigned to the cationic pyridinium counterpart of the salt.

Despite the fact that compound **5a** could not be fully purified, its structure could be deduced unambiguously on the basis of its spectroscopic characteristics and their similarity with those reported for the isostructural compound $(\mu\text{-H})\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^2\text{-CH}_3\text{C}=\text{NCH}_2\text{CH}_3]$, which has been characterised crystallographically [19]. The FD mass spectrum of **5a** showed an isotopic pattern characteristic for the presence of three ruthenium atoms around $m/e = 682$ (based on the ^{101}Ru -peak), corresponding to a stoichiometry of $\text{Ru}_3(\text{CO})_9(\text{iPr-SAI} + 2\text{H})$. The distribution of the 17 hydrogen atoms over the ligand and metal core could readily be inferred from ^1H NMR. A singlet resonance is found at -17.84 ppm, indicating the presence of a bridging hydride. The septet at 4.04 ppm and doublet at 0.99 ppm are mutually cou-

pled and can be ascribed to the isopropyl substituent at nitrogen. The remaining resonances were mutually connected. Decoupling experiments revealed the occurrence of a $(\text{CH}_3)_2\text{C}(\text{H})\text{CH}_2$ -fragment. So the structural formula for **5a** can be written as $(\mu\text{-H})\text{Ru}_3(\text{CO})_9[(\text{CH}_3)_2\text{C}(\text{H})\text{CH}_2\text{-C}=\text{N-iPr}]$. Interestingly, both the methylene protons and the methyl protons of the two isopropyl units of **5a** lack diastereotopicity in ^1H NMR, indicating either the presence of a centre of symmetry or fluxional behaviour. The latter is more likely as it has been reported that the $5e^-$ -donating imine ligand in $(\text{H})\text{Ru}_3(\text{CO})_9[\text{CH}_3\text{C}=\text{NCH}_2\text{CH}_3]$ is fluxional in solution, as a result of which the ^1H NMR signal for the methylene protons lacks diastereotopicity [19]. The fluxional process in this complex has been described as a restricted oscillatory motion of the organic ligand, coupled to hydride edge hopping and axial–radial CO-exchange on two of the three ruthenium atoms. The carbonyl IR-bands of $(\text{H})\text{Ru}_3(\text{CO})_9[\text{CH}_3\text{C}=\text{NCH}_2\text{CH}_3]$ in cyclohexane solution are found at 2091(m), 2064(s), 2036(vs), 2020(s), 2007(m), 2002(m), 1996(m), 1977(br) cm^{-1} . Both the frequencies and their intensities are very similar to those found for **5a** in hexane solution, indicating structural equivalency.

The molecular structure of **6b** is shown in Fig. 3. Selected bond lengths and angles are given in Table 4. This dinuclear ruthenium complex also features the well-known ‘saw-horse’ $\text{Ru}_2(\text{CO})_6$ core, in which the ruthenium atoms are bridged by a $6e^-$ -donating $\mu^2\text{-}\eta^3$ -allyl-aminocarbene ligand that was formed by double metallation (C_m and C_r -atoms) and dehydrogenation (-2H) of a *t*-butylsenecialdimine molecule. Formally, the metallacycle composed of the atoms Ru(1)–C(7)–C(8)–C(9)–C(10) constitutes a ruthenacyclopentadiene unit. In contrast to the commonly encountered η^2 -coordination mode for metallacyclopentadiene moieties, the ruthenacyclopentadiene unit in **6b** is η^4 -coordinated. There is no bonding interaction between Ru(2) and C(7); the Ru(2)–C(7) distance amounts to 2.614(3) Å. This can be attributed to the presence of the amino-substituent on C(7) causing redistribution of electrons over the ligand skeleton. The N–C(7) bond of 1.326(4) Å clearly indicates partial double bond character. Donation of electrons of the nitrogen lone pair to C(7) is further established by the planar geometry around the N(1) atom. These structural characteristics point to a significant carbene character of C(7). A similarly coordinated type of allyl-aminocarbene ligand is present in $\text{Fe}_2(\text{CO})_9[\text{C}(\text{C}_6\text{H}_5)_2\text{C}(\text{C}_6\text{H}_5)_2\text{C}(\text{H})\text{CN}(\text{H})\text{-}t\text{-Bu}]$, which was formed in a reaction of the zaaallylidene complex $\text{Fe}_2(\text{CO})_9[\text{C}(\text{H})\text{C}(\text{H})=\text{N}(\text{H})\text{-}t\text{-Bu}]$ with diphenylacetylene (the authors, however, make no notice of this specific structural aspect of this complex, for which an X-ray crystal structure has been determined; see Ref. [20]). These amino-substituted metallacyclopentadiene

Table 3
Selected bond distances (Å) and bond angles (deg) of 4a

<i>Residue 1</i>			
Ru(1)–Ru(2)	2.8935(9)	Ru(4)–C(10)	1.875(7)
Ru(1)–Ru(3)	2.8380(9)	Ru(4)–C(11)	1.892(7)
Ru(1)–Ru(4)	2.9277(9)	Ru(4)–C(12)	1.894(7)
Ru(1)–Ru(5)	2.8707(9)	Ru(5)–C(13)	1.864(7)
Ru(2)–Ru(3)	2.9091(9)	Ru(5)–C(14)	1.879(7)
Ru(2)–Ru(5)	2.8577(9)	Ru(5)–C(15)	1.890(7)
Ru(2)–Ru(6)	2.8428(9)	Ru(6)–C(16)	1.874(7)
Ru(3)–Ru(4)	2.881(9)	Ru(6)–C(17)	1.870(8)
Ru(3)–Ru(6)	2.8798(9)	Ru(6)–C(18)	1.869(8)
Ru(4)–Ru(5)	2.8512(9)		
Ru(4)–Ru(6)	2.8538(9)	C(1)–O(1)	1.136(9)
Ru(5)–Ru(6)	2.9504(9)	C(2)–O(2)	1.135(9)
		C(3)–O(3)	1.149(9)
Ru(1)–H(1)	2.03(6)	C(4)–O(4)	1.134(8)
Ru(2)–H(1)	2.03(6)	C(5)–O(5)	1.126(9)
Ru(3)–H(1)	2.03(6)	C(6)–O(6)	1.152(9)
Ru(4)–H(1)	2.03(6)	C(7)–O(7)	1.143(9)
Ru(5)–H(1)	2.01(6)	C(8)–O(8)	1.141(10)
Ru(6)–H(1)	2.06(6)	C(9)–O(9)	1.144(11)
		C(10)–O(10)	1.142(8)
Ru(1)–C(1)	1.892(7)	C(11)–O(11)	1.139(9)
Ru(1)–C(2)	1.884(7)	C(12)–O(12)	1.139(8)
Ru(1)–C(3)	1.875(7)	C(13)–O(13)	1.145(10)
Ru(2)–C(4)	1.881(6)	C(14)–O(14)	1.149(9)
Ru(2)–C(5)	1.895(7)	C(15)–O(15)	1.136(8)
Ru(2)–C(6)	1.872(7)	C(16)–O(16)	1.136(9)
Ru(3)–C(7)	1.876(7)	C(17)–O(17)	1.147(11)
Ru(3)–C(8)	1.862(8)	C(18)–O(18)	1.143(10)
Ru(3)–C(9)	1.868(8)		
Ru(2)–Ru(1)–Ru(3)	61.00(3)	Ru(1)–Ru(4)–Ru(3)	58.41(3)
Ru(2)–Ru(1)–Ru(4)	88.38(3)	Ru(1)–Ru(4)–Ru(5)	59.55(3)
Ru(2)–Ru(1)–Ru(5)	59.44(3)	Ru(1)–Ru(4)–Ru(6)	89.87(3)
Ru(3)–Ru(1)–Ru(4)	60.10(3)	Ru(3)–Ru(4)–Ru(5)	90.45(3)
Ru(3)–Ru(1)–Ru(5)	91.07(3)	Ru(3)–Ru(4)–Ru(6)	60.20(3)
Ru(4)–Ru(1)–Ru(5)	58.90(3)	Ru(5)–Ru(4)–Ru(6)	62.28(3)
Ru(1)–Ru(2)–Ru(3)	58.56(3)	Ru(1)–Ru(5)–Ru(2)	60.68(3)
Ru(1)–Ru(2)–Ru(5)	59.88(3)	Ru(1)–Ru(5)–Ru(4)	61.55(3)
Ru(1)–Ru(2)–Ru(6)	90.78(3)	Ru(1)–Ru(5)–Ru(6)	89.09(3)
Ru(3)–Ru(2)–Ru(5)	89.90(3)	Ru(2)–Ru(5)–Ru(4)	90.59(3)
Ru(3)–Ru(2)–Ru(6)	60.08(3)	Ru(2)–Ru(5)–Ru(6)	58.58(3)
Ru(5)–Ru(2)–Ru(6)	62.34(3)	Ru(4)–Ru(5)–Ru(6)	58.90(3)
Ru(1)–Ru(3)–Ru(2)	60.44(3)	Ru(2)–Ru(6)–Ru(3)	61.10(3)
Ru(1)–Ru(3)–Ru(4)	61.49(3)	Ru(2)–Ru(6)–Ru(4)	90.84(3)
Ru(1)–Ru(3)–Ru(6)	91.16(3)	Ru(2)–Ru(6)–Ru(5)	59.08(3)
Ru(2)–Ru(3)–Ru(4)	88.84(3)	Ru(3)–Ru(6)–Ru(4)	60.49(3)
Ru(2)–Ru(3)–Ru(6)	58.82(3)	Ru(3)–Ru(6)–Ru(5)	88.66(3)
Ru(4)–Ru(3)–Ru(6)	59.31(3)	Ru(4)–Ru(6)–Ru(5)	58.81(3)
Ru(1)–C(1)–O(1)	174.5(6)	Ru(4)–C(10)–O(10)	173.8(6)
Ru(1)–C(2)–O(2)	174.9(6)	Ru(4)–C(11)–O(11)	175.4(6)
Ru(1)–C(3)–O(3)	176.37(6)	Ru(4)–C(12)–O(12)	175.0(6)
Ru(2)–C(4)–O(4)	174.8(6)	Ru(5)–C(13)–O(13)	174.4(7)
Ru(2)–C(5)–O(5)	175.5(6)	Ru(5)–C(14)–O(14)	174.4(7)
Ru(2)–C(6)–O(6)	176.0(6)	Ru(5)–C(15)–O(15)	175.8(6)
Ru(3)–C(7)–O(7)	174.8(7)	Ru(6)–C(16)–O(16)	175.4(6)
Ru(3)–C(8)–O(8)	175.0(7)	Ru(6)–C(17)–O(17)	173.2(7)
Ru(3)–C(9)–O(9)	175.7(8)	Ru(6)–C(18)–O(18)	173.9(6)
<i>Residue 2</i>			
N(1)–C(19)	1.335(8)	C(21)–C(23)	1.371(9)
N(1)–C(24)	1.354(7)	C(23)–C(24)	1.377(8)

Table 3 (continued)

Residue 2			
N(1)–C(29)	1.509(8)	C(24)–C(25)	1.472(8)
C(19)–C(20)	1.360(9)	C(25)–C(26)	1.310(9)
C(20)–C(21)	1.391(9)	C(26)–C(27)	1.490(10)
C(21)–C(22)	1.498(10)	C(26)–C(28)	1.497(11)
C(19)–N(1)–C(24)	120.7(5)	C(21)–C(23)–C(24)	122.8(6)
C(19)–N(1)–C(29)	118.2(5)	C(23)–C(24)–N(1)	118.0(5)
C(24)–N(1)–C(29)	121.0(5)	C(23)–C(24)–C(25)	122.1(5)
N(1)–C(19)–C(20)	122.0(6)	C(24)–C(25)–C(26)	127.7(5)
C(19)–C(20)–C(21)	119.6(6)	C(25)–C(26)–C(27)	124.5(6)
C(20)–C(21)–C(22)	121.0(6)	C(25)–C(26)–C(28)	119.9(6)
C(20)–C(21)–C(23)	116.9(6)	C(27)–C(26)–C(28)	115.6(6)
C(22)–C(21)–C(23)	122.1(6)		

complexes (Fig. 4, type B) constitute structural intermediates between the classic η^5 -coordinated metallocyclopentadiene complexes (type A) and the novel σ - η^2 -coordinated bis-amino-substituted metallacyclopentadiene complex $\text{Os}_3(\text{CO})_{11}[\mu\text{-N}(\text{CH}_3)_2\text{CC}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CN}(\text{CH}_3)_2\text{K} \mu_3\text{-S}]$ [21], which contains two aminocarbene units, in combination with a π -coordinated olefin moiety (type C).

The carbene character of C(7) is clearly reflected by its ^{13}C NMR chemical shift of 211.3 ppm. This is comparable to the chemical shift of the aminocarbene carbon atom in $\text{Fe}_2(\text{CO})_6[\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{H})\text{CN}(\text{H})\text{-t-Bu}]$ of 213.3 ppm [19] and in the range of 200–240 ppm where metal carbene resonances are usually observed [22–24]. The IR frequency of the N–H proton of **6b** is found at 3420 cm^{-1} .

3.3. Possible formation pathways of the complexes

By using the SAI ligand (as opposed to MAD) cyclometallation of C_β is effectively blocked, and in-

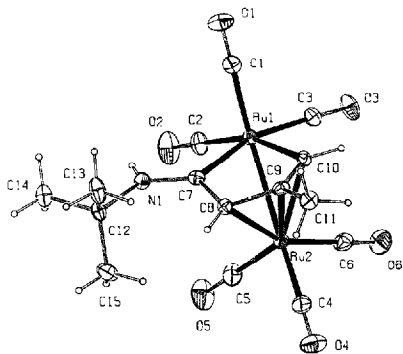


Fig. 3. Thermal ellipsoid plot of **6b** drawn at the 40% probability level, with the adopted numbering scheme.

deed cyclometallation at C_α , with formation of **2**, has become the dominant reaction. This enables us to study the reactivity of this azaallyl compound in more detail [4]. A likely reaction pathway leading to **2**, involving σ -N coordination of SAI to a coordinatively unsaturated ruthenium carbonyl centre followed by C_β -H activation on an adjacent ruthenium centre and subsequent transfer of the abstracted hydride back to the ligand, has been described previously [3].

During formation of the allyl-imine ligand in **3**, the parent SAI molecule has been doubly metallated at the C_γ -atom. Most likely the first C–H activation is facilitated by coordination of the senecialdimine via its lone pair on nitrogen to an unsaturated ruthenium carbonyl fragment (Scheme 3). Subsequent cyclometallation leads

Table 4
Selected bond distances (Å) and bond angles (deg) of **6b**

Ru(1)–Ru(2)	2.7449(7)	Ru(2)–C(6)	1.914(2)
Ru(1)–C(7)	2.085(2)	Ru(2)–C(5)	1.913(3)
Ru(1)–C(10)	2.075(3)	Ru(2)–C(4)	1.924(3)
Ru(1)–C(3)	1.945(2)	N(1)–C(12)	1.496(3)
Ru(1)–C(1)	1.899(2)	N(1)–C(7)	1.326(4)
Ru(1)–C(2)	1.940(3)	C(7)–C(8)	1.440(4)
Ru(2)···C(7)	2.614(3)	C(8)–C(9)	1.448(4)
Ru(2)–C(8)	2.245(2)	C(9)–C(10)	1.402(3)
Ru(2)–C(9)	2.227(3)	C(9)–C(11)	1.502(4)
Ru(2)–C(10)	2.217(2)		
Ru(2)–Ru(1)–C(1)	145.36(8)	C(6)–Ru(2)–C(13)	92.17(10)
Ru(2)–Ru(1)–C(2)	108.62(7)	C(7)–N(1)–C(12)	131.8(2)
Ru(2)–Ru(1)–C(3)	100.59(8)	N(1)–C(7)–C(8)	122.1(2)
Ru(2)–Ru(1)–C(7)	63.81(7)	Ru(1)–C(7)–N(1)	125.4(2)
Ru(2)–Ru(1)–C(10)	52.56(7)	Ru(1)–C(7)–C(8)	112.31(17)
C(2)–Ru(1)–C(10)	161.18(10)	Ru(2)–C(8)–C(7)	87.51(15)
C(3)–Ru(1)–C(7)	164.37(10)	Ru(2)–C(8)–C(9)	70.44(14)
C(7)–Ru(1)–C(10)	79.54(10)	C(7)–C(8)–C(9)	115.7(2)
Ru(1)–Ru(2)–C(4)	164.63(8)	C(8)–C(9)–C(10)	113.5(2)
Ru(1)–Ru(2)–C(5)	93.36(8)	C(8)–C(9)–C(11)	121.1(2)
Ru(1)–Ru(2)–C(6)	93.10(8)	C(10)–C(9)–C(11)	125.3(2)
Ru(1)–Ru(2)–C(8)	71.69(7)	Ru(2)–C(9)–C(11)	127.12(17)
Ru(1)–Ru(2)–C(9)	72.55(7)	Ru(1)–C(10)–Ru(2)	79.45(9)
Ru(1)–Ru(2)–C(10)	47.99(7)	Ru(1)–C(10)–C(9)	116.07(18)
C(3)–Ru(2)–C(10)	141.17(10)	Ru(2)–C(10)–C(9)	71.99(14)
C(6)–Ru(2)–C(8)	156.00(10)		

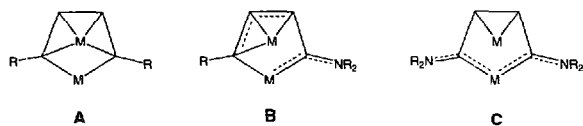
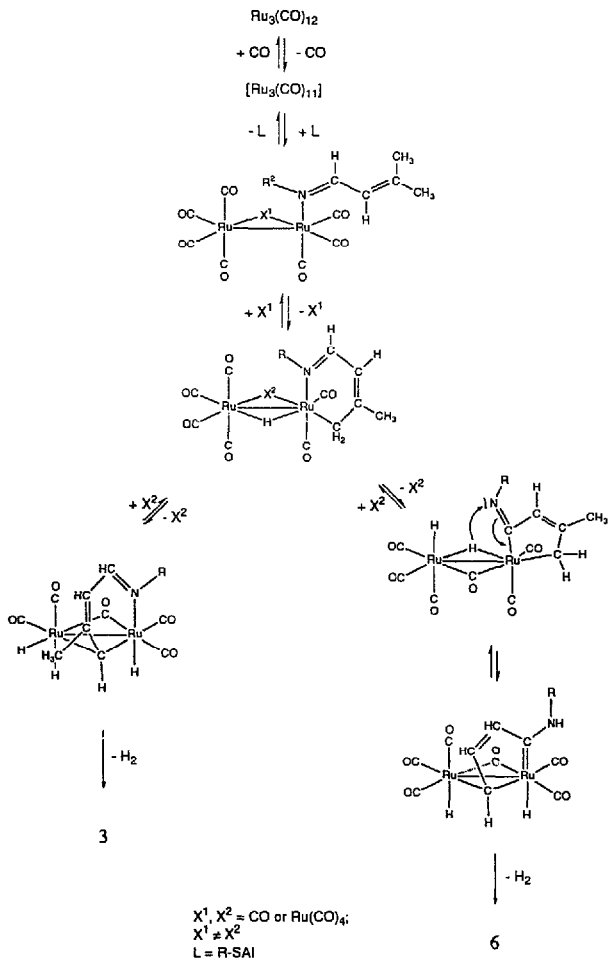


Fig. 4. Coordination behaviour of some metallacycles in dinuclear complexes.

Scheme 3. Proposed stepwise formation of **3** and **6** from senecialdime and $\text{Ru}_3(\text{CO})_{12}$.

to the six atom membered azaruthenacyclohexadiene unit. The second C_{γ} -H metallation will take place on an adjacent ruthenium centre and results in the formation of **3** after reductive elimination of H_2 .

The formation of the pyridinium ion in **4a** is the result of the coupling of two SAI molecules in a complex sequence of C-H and C-N bond activation and C-N and C-C bond formation processes. Overall net elimination of one molecule of isopropylamine has taken place. There are several possible reaction paths leading to the formation of this pyridinium ion. As no intermediates have been identified, no attempt will be made to speculate about the one that actually occurred. However, the crucial reaction step, in which the two senecialdimine molecules are connected via C-C and C-N coupling, may well have proceeded via a [4 + 2]-cycloaddition.

During formation of **5a** the olefin moiety of the SAI ligand has been hydrogenated and the imine C-H bond has been metallated. The source of the hydrogen taken up by **5a** is most likely the hydrogen that is liberated during formation of the complexes **3a** and **4a**, which both contain a dehydrogenated SAI ligand.

Compound **6** is formed for $R = t\text{-Bu}$, but not for $R = i\text{Pr}$ as indicated by ^1H NMR spectra of crude reaction mixtures. This suggests that metallation of C_{im} leading to **6** is triggered by the presence of the bulky $t\text{-Bu}$ substituent on the adjacent N-atom. A likely reaction pathway leading to **6** is given in Scheme 3: metallation of C_{γ} takes place after initial coordination of the SAI ligand via its lone pair on nitrogen to a coordinatively unsaturated ruthenium carbonyl unit. Subsequently, metallation of C_{im} may take place after breaking of the Ru-N bond. This crucial labilisation of the Ru-N bond is clearly enhanced by the presence of a bulky $t\text{-Bu}$ substituent. Hydride transfer to the imine N-atom and second metallation of C_{γ} and elimination of H_2 , results in the formation of **6**.

4. Conclusions

Substitution of the H_{β} -atom by a methyl group effectively blocks metallation of the C_{β} -atom of the monoazadiene during thermal reactions with $Ru_3(CO)_{12}$. Metallation of the C_{α} -atom has become the kinetically favoured reaction, whereas also metallation of the C_{im} and C_{γ} -atoms is observed. One of the γ -metallated organometallic products contains a novel μ_2 - η^3 -allyl-aminocarbene ligand, the second of this type reported thus far. The unusual geometry of this molecule is the result of electron delocalisation of the amino lone pair over the molecule. In addition a trisubstituted pyridinium moiety has been formed from two monoazadienes.

5. Supplementary material available

Tables of final atomic coordinates and equivalent isotropic thermal parameters and further details of the crystal structure determinations can be obtained from one of the authors (A.L.S.).

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References

- [1] C.J. Elsevier, W.P. Mul and K. Vrieze, *Inorg. Chim. Acta*, 198–200 (1992) 689.
- [2] W.P. Mul, C.J. Elsevier and J. Spaans, *J. Organomet. Chem.*, 402 (1991) 125.
- [3] W.P. Mul, C.J. Elsevier, L.H. Polm, K. Vrieze, M.C. Zoutberg, D. Heijdenrijk and C.H. Stam, *Organometallics*, 10 (1991) 2247.
- [4] O.C.P. Beers, J.C.P. Delis, W.P. Mul, C.J. Elsevier, K. Vrieze, W.J.J. Speck and A.L. Spek, *Inorg. Chem.*, 32 (1993) 3640.
- [5] H.R. Schullien, *Int. J. Mass Spectrosc. Ion Phys.*, 32 (1979) 97.
- [6] O. Doebner and W. von Miller, *Chem. Ber.*, 16 (1883) 1664.
- [7] H.C. Barany, E.A. Braude and M. Pianka, *J. Chem. Soc.*, (1949) 1898.
- [8] C.R. Eady, P.F. Jackson, B.F.G. Johnson, J. Lewis, M.C. Malatesta, M. McPartlin and W.J.H. Nelson, *J. Chem. Soc. Dalton Trans.*, (1980) 383.
- [9] A.L. Spek, *J. Appl. Crystallogr.*, 21 (1988) 578.
- [10] N. Walker and D. Stuart, *Acta Crystallogr. Sect. A.*, 39 (1983) 158.
- [11] G.M. Sheldrick, *SHELXL86 Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1986.
- [12] A.J.C. Wilson (ed.), *International Tables for Crystallography*, Vol. C, Kluwer, Dordrecht, 1992.
- [13] G.M. Sheldrick, *SHELXS93 Program for Crystal Structure Determination*, University of Göttingen, Germany, 1993.
- [14] A.L. Spek, *Acta Crystallogr. Sect. A.*, 46 (1990) C34.
- [15] L.H. Polm, W.P. Mul, C.J. Elsevier, K. Vrieze, M.J.N. Christophersen and C.H. Stam, *Polyhedron*, 7 (1988) 2521.
- [16] W.P. Mul, C.J. Elsevier, L.H. Polm, K. Vrieze, M.C. Zoutberg, D. Heijdenrijk and C.H. Stam, *Organometallics*, 10 (1991) 2447.
- [17] L.H. Polm, W.P. Mul, C.J. Elsevier, K. Vrieze, M.J.N. Christophersen and C.H. Stam, *Organometallics*, 7 (1988) 423.
- [18] P.L. Rodrigue, M. van Meerssche and P. Piret, *Acta Crystallogr. Sect. B.*, 25 (1969) 519.
- [19] S. Aime, R. Gobetto, F. Padova, M. Botta, E. Rosenberg and R.W. Gellert, *Organometallics*, 6 (1987) 2074.

- [20] T.E. Snead, C.A. Mirkin, K.-I. Lu, S.-B.T. Nguyen, W.-C. Teng, H.L. Beckman, G.L. Geoffroy, A.L. Rheingold and B.S. Haggerty, *Organometallics*, **11** (1992) 2613.
- [21] R.D. Adams, G. Chen, S. Sun, J.T. Tanner and T.A. Wolfe, *Organometallics*, **9** (1990) 251.
- [22] D.J. Carlin, B. Setinkaya and M.F. Lappert, *Chem. Rev.*, **72** (1972) 545.
- [23] M.A. Gallop and W.R. Roper, *Adv. Organomet. Chem.*, **25** (1986) 121.
- [24] W.R. Roper, *J. Organomet. Chem.*, **300** (1986) 167.