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Ruthenium complexes with diazadienes

XI *. Synthesis of alkyl, acyl, silyl and hydrido complexes via nucleophilic iodo-ruthenates(0). Crystal structure of (dad)(η^4-norbornadiene)methyliodoruthenium (dad = glyoxalbis(isopropylimine))

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Abstract

The preparation is described of a series of new ruthenium organic compounds [(dad)Ru(L)$_2$(E)I] (dad = diazadiene: RN=CR′CR′=NR; L = CO, L$_2$ = norbornadiene) with E = R, H, COR, or SiMe$_3$. Dihaloruthenium(II) diazadiene complexes are reduced in the presence of iodide to give nucleophilic Ru^0 intermediates [(dad)Ru(L)$_2$I]$^-$. These react with electrophiles to give stable Ru^{II} complexes, which are kinetically stable. The crystal structure of [(dad)Ru(nor-C$_7$H$_8$)(CH$_3$)I] (**12a**), (dad = glyoxalbis(isopropylimine)] has been determined. The methyl group is in a *cis*-disposition with respect to the dad and the norbornadiene. The salient structural feature is a bent I–Ru–CH$_3$ back-bone (angle C–Ru–I 161.6(4)°) with comparatively long bond distances (*d*(Ru–C) 2.222(13); *d*(Ru–I) 2.878(1) Å.

Introduction

Anionic complexes of metals in low oxidation states are frequently used in the synthesis of organometallic compounds. The metallates usually contain carbonyl and/or polyhapto coordinated olefin ligands, which are π-acidic and thus lower the electron density on the metal atom. In the iron triad anions of the type [CpM(CO)$_2$]$^-$ and [M(CO)$_4$]$^{2-}$ (M = Fe, Ru) are important [1–6]. Another group of metallates

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* For part X see ref. 38, for part IX see ref. 23.

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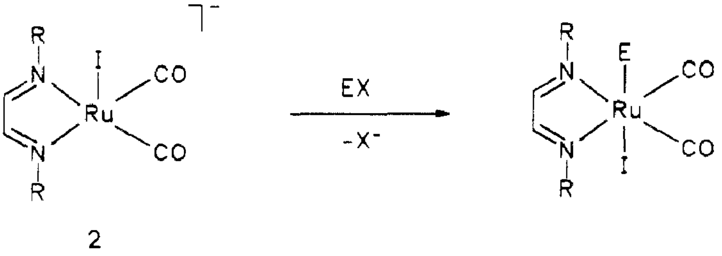
comprises hydrido species e.g. salts of $[HM(CO)_4]^-$ [2,7,8]. Analogous to these hydrido metallates are the well known acyl [3,9,10], alkyl [3] or silyl [11] ferrates. These anionic species have been well studied, but little is known about low valent metallates of the Group VIIIa elements containing halide or pseudohalide ligands. Except for a few early examples of isolated species $[Fe(CO)_4X]^-$ [12,13] such anions have been detected only in the gas phase or by electrochemical methods in solution [14,15]. Recently we reported on the electrochemistry of the diazadiene ruthenium complexes $[(dad)Ru(CO)_2I_2]$ (**1**) (dad = diazadiene: RN=CR′CR′=NR). The electrochemical features indicated that the anion $[(dad)Ru(CO)_2I]^-$ (**2**) is the initial product of the reduction [16]. In the same paper we described some preliminary preparative applications of these intermediates. Since then we have succeeded in using the ruthenates **2** in the synthesis of a series of novel ruthenium organic compounds containing the dad *N*-donor ligands. These complexes may serve as suitable compounds for the investigation of olefin oligomerisation, hydrogenation, and hydrosilylation reactions catalyzed by iron and ruthenium diazadiene complexes [17–20].

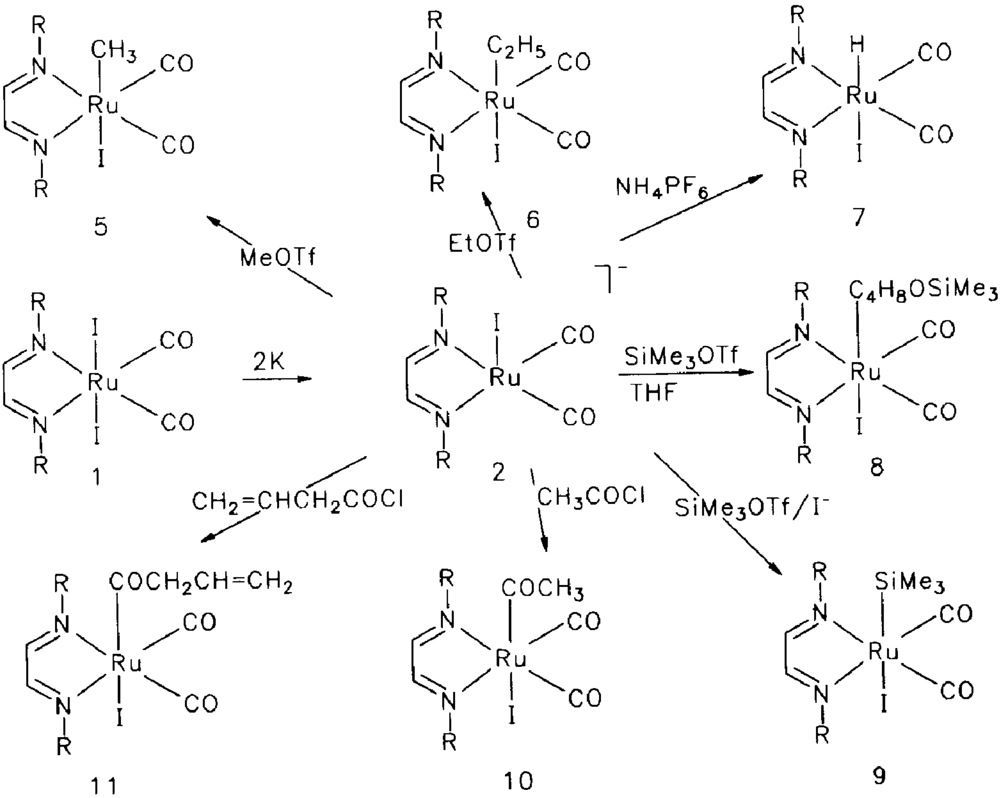
Results and discussion

Synthesis and reactions

The complexes $[(dad)Ru(L)_2X_2]$ (**1**: L = CO, X = I; **3**: L_2 = norbornadiene, X = Cl) are readily reduced by potassium sand or potassium naphthalenide in tetrahydrofuran. When X is iodide and/or in the presence of an excess of added lithium iodide the reduction yields iodide-containing ruthenates(0) such as **2**, which were identified by electrochemical methods [16]. Nucleophilic substitution of X in substrates EX (E = electrophile) by **2** yields the corresponding addition products (eq. 1):



Usually these reactions are carried out at −78 °C with potassium naphthalenide as the reducing agent. After the addition of the electrophile the mixture is allowed to warm to room temperature. The nucleophilic substitution sets in either at dry ice temperature or during the warming up. The yields are poor for dicarbonyl species **1** bearing small substituents on the imine N-atoms of the diazadiene ligand, owing to side reactions. One of the by-products is the known dimer $[(dad)Ru(CO)_2]_2$ [16,21]. In these cases the yields of addition products can be increased considerably by the addition of an excess of lithium iodide if strong electrophiles such as methyltriflate are used. The methylruthenium complexes **5** are obtained in quite good yield. The ethyl derivative **6b** is kinetically inert with respect to β-hydrogen transfer and olefin elimination, and so is complex **8**. These complexes also do not undergo carbonyl insertion when exposed to carbon monoxide at normal pressure. The acyl complexes are obtained directly from **2** by treatment with acyl chlorides. The reactions



Scheme 1

performed so far with the ruthenates $[(dad)Ru(CO)_2I]^-$ (**2**), which give the products **5**–**11**, are summarized in Scheme 1. The silylation of **2** with trimethylsilyl triflate in thf to form **9** is only a side reaction even in the presence of an excess of iodide. The main product **8**, a δ-siloxybutyl compound, results from the cleavage of tetrahydrofuran by the silyl triflate.

The reduction of $[(dad)Ru(nbd)Cl_2]$ (**3a**) in the presence of a tenfold excess of LiI gives an iodoruthenate(0) $[(dad)Ru(nbd)I]^-$ (**4**), which adds methyl triflate to form the methyl complex $[(dad)Ru(nbd)(CH_3)I]$ (**12a**) (eq. 2). In a side reaction $[(dad)Ru(nbd)I_2]$ (**13a**) is formed, indicating that the electrophile is reduced in part by the intermediate **4**.

3 12

The new ruthenium organic compounds, like the dihalocomplexes **1** and **3** [16], are sensitive toward visible light. The reactions are complex and not yet well understood. Irradiation of **11b** with visible light in dichloromethane gave a mixture of products. A monocarbonyl complex, which had lost the allyl group, was isolated.

The desired π-allyl compound is not accessible by this method, but can be prepared by a different route [22].

With the exception of **7b** all the complexes described here are stable and kinetically inert. The hydrido complex decomposes in chloroform solution. The ^{1}H NMR spectra of **7b** in $CDCl_3$ indicate the occurrence of a H^-/Cl^--exchange to give $CDHCl_2$. From $CHCl_3$ solutions three different products were isolated, two of which were identified as the diiodo compound **1b** and the mixed dihalocomplex $[(dad)Ru(CO)_2ICl]$ (**14b**).

Electrochemical studies of the reduction of the complexes **5**–**11** indicate the formation of species $[(dad)Ru(CO)_2E]$ (isolobal with CH_3) and $[(dad)Ru(CO)_2E]^-$ (isolobal with CH_3^-), which may serve as intermediates for introducing the (dad)Ru unit deliberately into transition metal clusters. Thus after the $1e^-$ reduction of **5a** the novel dinuclear complex $[(dad)Ru(CO)_2(CH_3)]_2$ could be isolated and structurally characterized [23].

^{1}H NMR spectra and structure

The use of prochiral *N*-substituents in the diazadiene ligands considerably facilitates the elucidation of the structures of all newly synthezised types of products by means of NMR spectroscopy. The ^{1}H NMR data in Table 1 show that all sets of isochronous protons of the free ligands, which do not lie in the diimine plane, split into two diastereotopic sets under the symmetry of the complex. Thus there is no plane of symmetry lying in the Ru(dad) plane, but there is one perpendicular to this, bisecting the diazadiene. The only structure consistent with this symmetry is the one with L_2 (2 CO or nbd) *trans* to the dad, as shown in the formulae. The *cis*-CO-arrangement is indicated by the infrared spectra of compounds **5**–**11**. The chemical shift values of the protons on the metal-bonded groups E agree with relevant literature data in most cases [19,24]. Only the proton resonance of the Ru-bonded methyl group in **12a** (δ 1.32 ppm) appears at considerably lower field than in the corresponding complexes **5** (δ -0.03 to 0.33 ppm). We were interested in the structure of such a complex, since a (dad)M(norbornadiene) moiety, with an alkyl group *cis* to the diene is a suggested intermediate in the very stereoselective *endo*-alkylation of norbornadiene by ethylene or in the acyclic coupling of olefins to give 1,3-dienes on (dad)iron(0) catalysts. An X-ray diffraction study was carried out on **12a**.

X-ray structure determination of $[(dad)Ru(nbd)(CH_3)I]$ (12a)

Suitable crystals of **12a** were obtained by recrystallizing the compound from dichloromethane/n-hexane. The positions of the heavy atoms were determined by a Patterson analysis [25]. All non-hydrogen atoms were refined anisotropically, and H atoms were placed in calculated positions [26]. Owing to some disorder, which we could not resolve, the bond parameters for the isopropyl groups could not be accurately determined, and so the interatomic distances between the relevant carbon atoms were fixed in calculated positions. Correction was made for absorption. Refinement by full-matrix least squares progressed to a final *R*-value of 0.0579 ($R_w = 0.0443$). Atomic coordinates are listed in Table 2. The molecular structure is depicted in Fig. 1, and important bond distances and angles are listed in Table 3.

The X-ray structure determination confirms the overall geometry, proposed on the basis of the ^{1}H NMR data. The bond distances and angles within the Ru(dad)

Table 1

^{1}H NMR data for complexes 5–13

No.	R′	R	E	δ (ppm) [a] and J(Hz) values	
				dad	Ru–E
5a	H	i-Pr	Me	8.16 (s, 2H); 4.49 (sept, 2H); 1.61 (d, ^{3}J 6.6, 6H); 1.58 (d, ^{3}J 6.5, 6H)	−0.03 (s,3H)
5b	H	CH(i-Pr)$_2$	Me	7.99 (s, 2H); 4.04 (dd, ^{3}J 6, 2H); 2.71 (dsept, 2H); 2.29 (dsept, 2H); 1.14 (d, ^{3}J 7.0, 6H); 1.07 (d, ^{3}J 7.0, 6H); 1.04 (d, ^{3}J 6.8, 6H); 1.03 (d, ^{3}J 6.8, 6H)	−0.02 (s,3H)
5c	Me	i-Pr	Me	4.46 (sept, 2H); 2.42 (s, 6H); 1.77 (d, ^{3}J 6.6, 6H); 1.42 (d, ^{3}J 6.7, 6H)	−0.03 (s,3H)
5d	H	*o,o′*-Me$_2$C$_6$H$_3$	Me	8.30 (s, 2H); 7.2 (m, 6H); 2.64 (s, 3H); 2.32 (s, 3H)	0.33 (s,3H)
6b	H	CH(i-Pr)$_2$	Et	7.96 (s, 2H); 4.04 (dd, ^{3}J 6, 2H); 2.84 (dsept, 2H); 2.32 (dsept, 2H); 1.17((d, ^{3}J 7.1, 6H); 1.07 (d, ^{3}J 6.9, 6H); 1.06 (d, ^{3}J 6.7, 6H); 1.01 (d, ^{3}J 6.9, 6H)	1.45 (tr, 3J 7.6, 3H); 0.85 (qrt, 2H)
7b	H	CH(i-Pr)$_2$	H	8.37 (s, 2H); 3.75 (dd, ^{3}J 4.8/8.5, 2H); 2.40 (dsept, ^{3}J 4.8/7, 2H); 2.38 (dsept, ^{3}J 8.5/7, 2H); 1.16 (d, ^{3}J 7.0, 6H); 1.12 (d, ^{3}J 7.0, 6H); 1.09 (d, ^{3}J 6.6, 6H); 1.08 (d, ^{3}J 6.6, 6H)	−9.22 (s, 1H) [b]
8a	H	i-Pr	BuOSiMe$_3$	8.15 (s, 2H); 4.52 (sept, 2H); 1.59 (d, ^{3}J 6.0, 6H); 1.57 (d, ^{3}J 6.0, 6H)	3.54 (tr, ^{3}J 6.7, 2H); 1.7 (m, 2H); 1.47 (m, 2H); 0.79 (AA′XX′, 2H); 0.09 (s, 9H)
8b	H	CH-i-Pr$_2$	BuOSiMe$_3$	7.96 (s, 2H); 4.03 (dd, ^{3}J 5/7, 2H); 2.85 (dsept, ^{3}J 5/7, 2H); 2.29 (dsept, ^{3}J 7, 2H); 1.17 (d, ^{3}J 7.1, 6H); 1.06 (d, ^{3}J 6.8, 6H); 1.05 (d, ^{3}J 6.9, 6H); 1.01 (d, ^{3}J 6.9, 6H)	3.55 (tr, ^{3}J 6.9, 2H); 1.85 (m, 2H); 1.54 (m, 2H) 0.75 (AA′XX′, 2H); 0.10 (s, 94)
9a	H	i-Pr	SiMe$_3$	8.21 (s, 2H); 4.58 (sept, 2H); 1.70 (d, ^{3}J 6.5, 6H); 1.52 (d, ^{3}J 7.0, 6H)	0.11 (s, 9H)
10b	H	CH-i-Pr$_2$	COCH$_3$	8.07 (s, 2H); 3.86 (dd, ^{3}J 3.2/8.9, 2H); 2.26 (dsept, ^{3}J 8.9/7, 2H); 1.96 (dsept, ^{3}J 3.2/7, 2H); 1.10 (d, ^{3}J 7.2, 6H); 1.05 (d, ^{3}J 6.8, 6H); 1.02 (d, ^{3}J 6.8, 6H); 0.97 (d, ^{3}J 7.0, 6H)	2.52 (s, 3H)
11b	H	CH(i-Pr)$_2$	CO(All)	8.06 (s, 2H); 3.87 (dd, ^{3}J 3.1/9.3, 2H); 2.31 (dsept, ^{3}J 9.3/7, 2H); 1.97 (dsept, ^{3}J 3.1/7, 2H); 1.10 (d, ^{3}J 7.3, 6H); 1.03 (d, ^{3}J 6.6, 6H);	5.78 (tdd, ^{3}J 7.2/10.1/17.1, 1H); 5.13 (ABX, $^{2}J_{AB}$ 1.5, $^{3}J_{AX}$ 10.1, 1H); 5.10 (ABX, $^{2}J_{AB}$ 1.5, $^{3}J_{BX}$ 17.1, 1H); 3.54 (dt, ^{3}J 7.2, ^{4}J 1.2, 2H)

Table 1 (continued)

No.	R′	R	E	δ (ppm) [a] and J(Hz) values	
				dad	Ru–E
11b	H	$CH(i\text{-}Pr)_2$	CO(All)	1.01 (d, ^{3}J 6.7, 6H); 0.90 (d, ^{3}J 7.0, 6H)	
12a	H	i-Pr	CH_3	8.01 (s, 2H); 3.55 (sept, 2H); 1.35 (d, ^{3}J 6.7, 6H); 1.18 (d, ^{3}J 6.6, 6H) nbd: 4.47 (tr, ^{3}J 4, 2H); 3.86 (br, 1H); 3.64 (br, 1H); 3.29 (tr, ^{3}J 4, 2H); 1.11 (dd, ^{3}J 1, 2H)	1.32 (s, 3H)
13a	H	i-Pr	I	8.00 (s, 2H); 3.65 (sept, 2H); 1.43 (d, ^{3}J 6.5, 12H); nbd: 4.98 (tr, ^{3}J 2.3, 4H); 3.8 (br, 2H); 1.26 (tr, ^{3}J 1, 2H)	

[a] Solvent $CDCl_3$. [b] Solvent $(CD_3)_2CO$.

moiety correspond to those for other Ru^{II}-diazadiene structures [27] and also to values for a similar ligand in the gas phase [28]. The bond parameters for the coordinated norbornadiene do not differ much from published data [29–32]. The most striking feature of this structure is the bent H_3C–Ru–I unit (161.6(4)°) with its rather long interatomic distances between the atoms. The Ru–I bond is 0.17 Å longer than the corresponding bond in complex **1** [27]. Compared with Ru–C bond lengths of 2.144 Å and 2.099 Å in similar complexes [29,33], the Ru–C12 distance of 2.222(13) Å is also elongated. This distortion, together with a descreening effect of the C=C double bonds of the norbornadiene, may be responsible for the appearance at low field of the signal from the C12 protons in the NMR spectrum. With respect to the Ru(dad) plane the distortion of the methyl group is even slightly larger than

Table 2

Atomic coordinates for **12a** (e.s.d's in parentheses)

Atom	x	y	z	U_{eq}
Ru	0.2287(1)	0.0320(1)	0.1646(1)	0.066(1)
I	0.0840(1)	−0.1178(1)	0.1724(1)	0.093(1)
N1	0.1004(8)	0.1177(7)	0.1489(6)	0.079(14)
N2	0.1872(9)	0.0642(6)	0.2635(6)	0.082(15)
C1	0.0644(12)	0.1488(9)	0.2067(9)	0.094(23)
C2	0.1161(12)	0.1202(10)	0.2676(8)	0.096(24)
C3	0.0649(11)	0.1289(11)	0.0793(10)	0.131(27)
C4	0.2407(14)	0.0350(9)	0.3230(6)	0.125(23)
C5	0.2596(11)	−0.0376(9)	0.0651(6)	0.080(17)
C6	0.3120(11)	0.0470(11)	0.0689(7)	0.086(20)
C7	0.3292(9)	−0.0938(9)	0.1711(9)	0.086(19)
C8	0.3841(9)	−0.0068(8)	0.1744(8)	0.086(18)
C9	0.3216(10)	−0.1187(11)	0.0947(7)	0.087(19)
C10	0.4116(12)	0.0166(9)	0.1001(8)	0.094(20)
C11	0.4228(13)	−0.0866(10)	0.0684(10)	0.110(25)
C12	0.3032(12)	0.1721(8)	0.1774(10)	0.098(20)

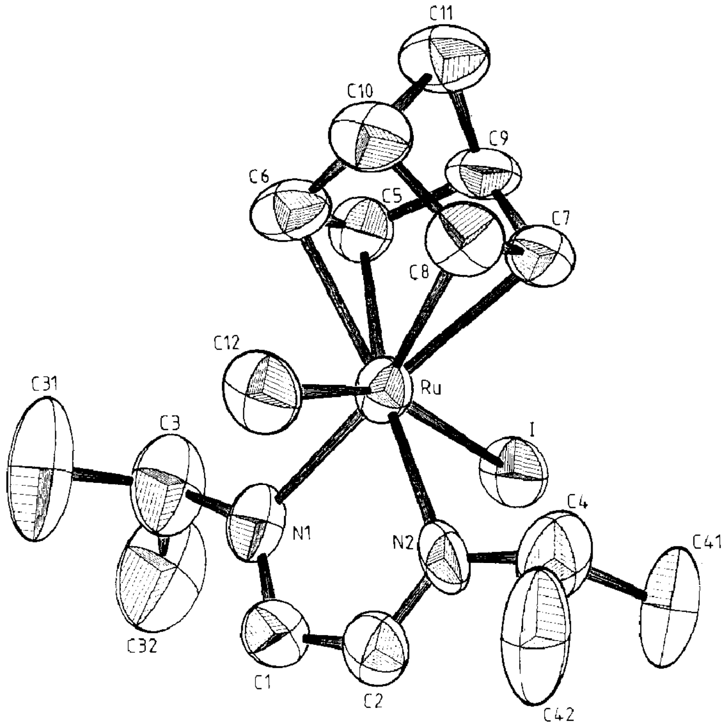


Fig. 1. ORTEP plot (33% probability) of the molecular structure of **12a** with atomic numbering scheme.

Table 3

Important bond lengths and angles in **12a** (e.s.d.'s in parentheses)

Bond lengths in Å		Bond angles in °	
Ru–I	2.878(1)	I–Ru–C12	161.59(39)
Ru–N1	2.137(10)	I–Ru–N1	82.06(28)
Ru–N2	2.051(12)	I–Ru–N2	85.67(31)
Ru–C5	2.203(12)	N1–Ru–N2	77.62(44)
Ru–C6	2.184(13)	N1–Ru–C12	83.67(40)
Ru–C7	2.232(12)	N2–Ru–C12	79.94(43)
Ru–C8	2.186(13)	C5–Ru–C7	65.44(47)
Ru–C12	2.222(13)	C6–Ru–C8	66.32(51)
N1–C1	1.298(20)	Ru–N1–C1	111.85(95)
N1–C3	1.444(22)	Ru–N2–C2	114.29(102)
N2–C2	1.246(19)	N1–C1–C2	115.82(135)
N2–C4	1.424(18)	N2–C2–C1	120.15(143)
C1–C2	1.431(23)	C6–C5–C9	109.50(118)
C5–C6	1.385(20)	C5–C6–C10	103.64(118)
C5–C9	1.526(20)	C8–C7–C9	105.83(114)
C6–C10	1.540(21)	C7–C8–C10	105.67(115)
C7–C8	1.429(17)	C8–Ru–C12	76.88(50)
C7–C9	1.528(22)	C7–Ru–C12	114.40(53)
C8–C10	1.525(22)	C7–Ru–C8	37.74(45)
C9–C11	1.533(23)	N2–Ru–C7	106.74(47)
C10–C11	1.580(20)	N2–Ru–C8	103.76(51)

that for the iodo ligand, indicating that the non-bonding radius of the methyl ligand is greater than that of the bonded iodide *.

Conclusions

The high nucleophilicity of the iodide is responsible for the formation of the iodoruthenates (**2**) [16]. In the case of chloro precursors **3**, the reduction leads to reactive species, which behave like four coordinate [(dad)Ru(nbd)] (probably in equilibrium with a solvated pentacoordinate moiety [19b]). In the presence of iodide, iodoruthenates(0) are again formed. Halometallates of zerovalent ruthenium can thus serve as an excellent source of various types of organometallic compounds, such as alkyl, acyl, hydride, and silyl derivatives. Their kinetic stability prevents the easy interconversion of several types of complexes (acyls ↔ alkyls; alkyls ↔ hydrides), which are related to each other by the typical reactions, involved in the hydroformylation of alkenes. They can also serve as models for intermediates in olefin isomerization, hydrogenation or hydrosilylation reactions, catalyzed by iron and/or ruthenium diazadiene complexes [17–20]. The distortion in the structure of **12a** shows that the methyl group is in very close contact with the norbornadiene carbon atoms C5/C6. A ready transfer of an organic group to the *endo* position of norbornadiene can thus be envisaged, as is the case in the stereo- and enantio-selective reaction of ethylene and norbornadiene to give *endo*-3-vinylnortricyclane in the presence of a (dad)iron(0) catalyst [34].

Experimental

All experiments and spectroscopic measurements were performed under nitrogen. NMR spectra were recorded on a Bruker WP80-SYFT or a Bruker AM360 instrument, and IR spectra on a Perkin Elmer Model 325 spectrometer. UV/VIS spectra were recorded with a Perkin Elmer spectrograph model 554. Details of experimental conditions for electrochemical studies have been given previously [16,24]. All solvents and reagents were carefully dried and kept under nitrogen. The starting materials **1** and **3** were prepared by published methods [27,35].

X-ray structural determination of **12a**: Molecular formula: $C_{16}H_{27}IN_2Ru$; Molecular mass of formula unit: 475.36 g/mol; crystal system: orthorhombic; space group *Pcab*; lattice constants: a 13.568(4), b 14.011(4), c 19.404(5) Å; V 3688.69(7) Å^3; $Z = 8$; D_{calc} 1.712 g/cm^3; μ(Mo-K_α) 23.24 cm^{-1}. Number of measured reflections 3687, of which 3267 were symmetry-independent. Number of reflections used, 1795; number of parameters refined, 208. Data collection by the $\theta/2\theta$-technique, with a 2θ-range from 4.5 to 50°. The $h/k/l$ range was 0/0/0 to 17/17/24. 15 computer-centered reflections from diverse regions of reciprocal space were chosen for determination of the cell parameters. Three control reflections (1/6/6; 7/1/3; 6/0/ – 6) were measured every hundred reflections to monitor any intensity changes. A Syntex-P2$_1$ diffractometer with graphite-monochromated Mo-K_α radiation (λ

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* Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54090, the names of the authors, and the journal citation.

0.70926 Å) was used. The final R value converged to 0.0579, R_w to 0.0430 ($w = x/[\sigma^2(F_o)]$; $x = 2.3968$). Maximum residual electron density 0.78 e/Å^3; maximum shift/e.s.d. 1.66 for the isopropyl groups (see text) and 0.38 for the other part of the structure. Bond lengths and angles, with standard deviations, were calculated by use of the program PARST 7 [36]. Plots of the crystal structure were obtained by use of ORTEP [37]. All calculations were performed on the Central University Computer, Siemens 7.882.

General procedure for the preparation of complexes

In a carefully dried Schlenk vessel 0.1 to 1.0 mmol of **1** or **3** are dissolved in 10 to 20 ml of tetrahydrofuran and the mixture is cooled to −78 °C in a dry ice/methanol bath. For the reduction two equivalents of a potassium naphthalenide solution in thf (usually ca. 0.1 *M*) are added. The colour of the mixture changes immediately from red orange to dark violet. One equivalent of the relevant electrophile EX is then added. The solution is allowed to warm to room temperature then separated from the precipitated potassium salts and the solvent evaporated off in vacuo. The products are separated from unreacted starting material and by-products by column chromatography on silica gel with dichloromethane as eluent. The band containing the product follows that containing the starting material and naphthalene. After evaporation of the solvents from the eluate the complexes are recrystallized from dichloromethane/hexane or, in the case of the acyl complexes, from ether/hexane.

*Dicarbonylglyoxalbis(isopropylimine)methyliodoruthenium (**5a**).* Alkylating agent: methyl triflate in the presence of a tenfold excess of lithium iodide. Yield, 83.5%. Analysis. Found: C, 30.03; H, 4.29; N, 6.25. $C_{11}H_{19}IN_2O_2Ru$ (439.24) calcd.: C, 30.08; H, 4.36; N, 6.37%. IR (KBr): ν(CO) 1945, 2030 cm^{-1}. UV/VIS (CH_2Cl_2), λ_{max} (nm ($\epsilon = cm^2 m M^{-1}$)): 460 (1700); 365 (2800); 290 (3600).

*Dicarbonylglyoxalbis(2,4-dimethylpent-3-ylimine)methyliodoruthenium (**5b**).* Alkylating agent: methyl triflate. Yield, 75.1%. Analysis. Found: C, 40.95; H, 6.25; N, 4.97. $C_{19}H_{35}IN_2O_2Ru$ (551.46) calcd.: C, 41.38; H, 6.40; N, 5.08%. IR (KBr): ν(CO) 1950, 2030 cm^{-1}.

*Dicarbonylbiacetylbis(isopropylimine)methyliodoruthenium (**5c**).* Alkylating agent: methyl triflate. Yield, 43.2%. Analysis. Found: C, 33.70; H, 4.97; N, 5.96. $C_{13}H_{23}IN_2O_2Ru$ (467.30) calcd.: C, 33.41; H, 4.96; N, 5.99%. IR (KBr): ν(CO) 1950, 2025 cm^{-1}. UV/VIS (CH_2Cl_2): λ_{max} (nm (ϵ cm^{2}mM^{-1})): 420 (2000); 344 (3200); 286 (5400).

*Dicarbonylglyoxalbis(2,6-dimethylphenylimine)methyliodoruthenium (**5d**).* Alkylating agent: methyl triflate; Yield: 44.4%. Analysis. Found: C, 43.02; H, 3.84; N, 4.69. $C_{21}H_{23}IN_2O_2Ru$ (563.39) calcd.: C, 44.77; H, 4.12; N, 4.97%. IR (KBr): ν(CO) 1970, 2050 cm^{-1}.

*Dicarbonylglyoxalbis(2,4-dimethylpent-3-ylimine)ethyliodoruthenium (**6b**).* Alkylating agent: ethyltriflate; Yield, 44.9%. Analysis. Found; C, 42.56; H, 7.84; N, 4.94. $C_{20}H_{37}IN_2O_2Ru$ (565.49) calcd.: C, 42.28; H, 6.60; N, 4.95%. IR (KBr): ν(CO) 1949, 2031 cm^{-1}.

*Dicarbonylglyoxalbis(2,4-dimethylpent-3-ylimine)hydridoiodoruthenium (**7b**).* Protonating agent: Ammonium hexafluorophosphate; Yield, 62.3%. Analysis. Found: C, 40.66; H, 6.24; N, 5.30. $C_{18}H_{33}IN_2O_2Ru$ (537.43) calcd.: C, 40.23; H, 6.19; N, 5.21%. IR (KBr): ν(CO) 1970, 2047 cm^{-1}. UV/VIS (CH_2Cl_2): λ_{max} (nm (ϵ cm^{2}mM^{-1})): 436 (2100); 336 (3000).

Dicarbonylglyoxalbis(isopropylimine)-4-trimethylsiloxybutyliodoruthenium (***8a***)

Alkylating agent: trimethylsilyl triflate in tetrahyrofuran, in the presence of a tenfold excess of lithium iodide. Yield; 23.7%. Analysis. Found: C, 35.53; H, 5.69; N, 4.97. $C_{17}H_{33}IN_2O_3RuSi$ (569.51) calcd.: C, 35.85; H, 5.84; N, 4.92%. IR (KBr); ν(CO) 1953, 2027 cm^{-1}.

Dicarbonylglyoxalbis(2,4-dimethylpent-3-ylimine)iodo-4-(trimethylsiloxy)butylruthenium (***8b***). Silylating agent, trimethylsilyl triflate in tetrahydrofuran; Yield: 31.7%. Analysis. Found: C, 43.99; H, 7.17; N, 4.31. $C_{25}H_{49}IN_2O_3RuSi$ (681.72) calcd.: C, 44.05; H, 7.25; N, 4.11%. IR (KBr): ν(CO) 1957, 2034 cm^{-1}.

Dicarbonylglyoxalbis(isopropylimine)iodotrimethylsilylruthenium (***9a***). Silylating agent: trimethylsilyl triflate in the presence of a tenfold excess of lithium iodide. Rapid reaction at −78° C. Yield, 5.6%. Analysis. Found: C, 31.55; H, 4.91; N, 6.13. $C_{13}H_{25}IN_2O_2RuSi$ (497.40) calcd.: C, 31.39; H, 5.07; N, 5.63%. IR (KBr): ν(CO) 1956, 2030 cm^{-1}. **9a** was obtained as a by-product of **8a**.

Acetyldicarbonylglyoxalbis(2,4-dimethylpent-3-ylimine)iodoruthenium (***10b***). Acylating agent; acetyl chloride. Yield, 72.2%. Analysis. Found: C, 41.35; H, 7.29; N, 3.79. $C_{20}H_{35}IN_2O_3Ru$ (579.47) calcd.: C, 41.46; H, 6.09; N, 4.83%. IR (KBr): ν(CO) 1662, 1970, 2040 cm^{-1}. UV/VIS (CH_2Cl_2): λ_{max} (nm (ϵ $cm^2 mM^{-1}$)): 484 (2100); 232 (21000).

3-Butenoyldicarbonylglyoxalbis(2,4-dimethylpent-3-ylimine)iodoruthenium (***11b***). Acylating agent: 3-butenoic acid chloride. Yield, 5.3%. Analysis. Found: C, 43.48; H, 6.38; N, 4.63. $C_{22}H_{37}IN_2O_3Ru$ (605.51) calcd.: C, 43.64; H, 6.16; N, 4.62%. IR (KBr): ν(CO) 1657, 1980, 2050 cm^{-1}.

Glyoxalbis(isopropylimine)-η^4-norbornadienemethyliodoruthenium (***12a***). Alkylating agent: methyl triflate, in the presence of a tenfold excess of lithium iodide. Yield 22.3%. The by-product **13a** (23.2%) was also isolated. Analysis. Found: C, 40.21; H, 5.65; N, 6.15. $C_{16}H_{27}IN_2Ru$ (475.36) calcd.: C, 40.43; H, 5.73; N, 5.89%.

Glyoxalbis(isopropylimine)-η^4-norbornadienediiodoruthenium (***13a***). Analysis. Found C, 30.78; H, 4.12; N, 5.03. $C_{15}H_{24}IN_2Ru$ (587.23) calcd.: C, 30.68; H, 4.12; N, 4.77%.

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