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RUTHENIUM COMPLEXES WITH DIAZADIENES

VIII *. DIAZADIENEDICARBONYL-RUTHENIUM(II) AND -RUTHENIUM(0) COMPLEXES: SYNTHESIS, PHOTOCHEMISTRY AND ELECTROCHEMISTRY **

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Summary

The easily accessible diazadieneruthenium carbonyl complexes [(DAD)Ru-$(CO)_2I_2$] (I, DAD = RN=CR′CR′=NR) are photolytically labile and undergo CO substitution. The reactions can be monitored by UV/VIS spectroscopy and by cyclic voltammetry (CV), in which there are points of constant current and potential analogous to isosbestic points. A CV study of the irreversible two-electron reduction of I has also been carried out, and found to give free iodide ion and the anionic intermediate $[(DAD)Ru(CO)_2I]^-$. This latter complex undergoes replacement of the iodide ligand by the solvent, carbon monoxide, or triphenylphosphine. The differences in reoxidation potentials and reversibility criteria provide information about the nature of the various electrochemically-formed ruthenium(0) complexes $[(DAD)Ru(CO)_2L]$ and their kinetic behaviour.

The outcome of chemical reduction of I in solutions of higher concentration depends on the steric effect of the DAD ligand; with smaller ligands the final products are the DAD-bridged dimers $[(DAD)Ru(CO)_2]$ (V). In the presence of phosphine or carbon monoxide the corresponding five-coordinate complexes IV and VI, $[(DAD)Ru(CO)_2L]$, are formed, and can be isolated and characterized spectroscopically. Addition of methyl iodide or an ammonium salt as a proton donor leads to oxidative addition products $[(DAD)Ru(CO)_2(CH_3)I]$ (VII) and [(DAD)Ru-$(CO)_2(H)I]$ (VIII). Photochemical substitution and reductive activation enable the introduction and elimination of ligands in a predictable manner.

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* For part VII see ref. 1.

** Dedicated to Professor J. Tirouflet on the occasion of his retirement.

Introduction

Most of the work on ruthenium complexes with unsaturated nitrogen ligands has involved bipyridylruthenium(II/III/IV) systems [2]. It has been shown, however, that 1,4-diaza-1,3-dienes (DAD) RN=CR′CR′=NR can stabilize many metals in low oxidation states [3].

A complex of the type [$Ru^0(DAD)_3$], produced by hydrogenation of [Ru(1,5-cod)(1,3,5-COT)] in the presence of DAD, has been characterized by X-ray diffraction [4]. Very stable complexes of the type [(DAD)Ru(arene)] [5], [(DAD)Ru(diene)L] [6] and [(DAD)Ru(triene)] [6] were recently described. Related species of the type [$(DAD)Fe(diene)_x$] are thought to be present during very selective catalytic reactions stereochemically controlled by the DAD ligands [7]. We were interested in low-valent (DAD)Ru complexes containing other monodentate ligands and decided to investigate coordinatively-unsaturated dicarbonyls by reduction of [$(DAD)Ru(CO)_2I_2$] complexes I [8]. The (DAD)Ru-carbonyl system seemed very promising since a number of fascinating structures with only these two ligands on ruthenium have been described by the groups of Van Koten and Vrieze [9,10]. However, all of these complexes are di- or oligo-nuclear.

Halides are rather poor ligands for zero-valent metals, and it seems reasonable to assume loss of iodide from I during reduction. However, cases have been reported in which electrochemical studies indicate reversible electron uptake, for example Cp_2MX_2 (M = Ti, Zr) [11]. In the case of complexes isoelectronic with I, such as [$(bipy)PtCl_2(CH_2)_3$], there is an irreversible two-electron transfer with the loss of both chloro ligands [12]. For the isocyanide complexes *trans*-[$(RNC)_2PtX_2$], even the first electron transfer is irreversible (loss of X^-) and the second leads to deposition of the metal [13]. The reduction of [$(terpy)Ru(dppe)Cl]^+$ is an irreversible two electron transfer process resulting in loss of chloride [14]. The reduction of [$(bipy)_2RuX_2$] is reported to be irreversible [15]. However, there are also examples of iodo ligands coordinated to zero-valent metals [16].

Since the carbonyl iodides I also exhibit strong CT absorptions in the visible region typical of closed-shell DAD complexes, and similar to that of bipy complexes, we decided to investigate the photochemistry and the electrochemistry of I as well as their chemical reduction.

Results and discussion

Photochemical behaviour of diazadienedicarbonyldiiodoruthenium

The complexes of the type [$(DAD)Ru(CO)_2I_2$] (I, DAD = 1,4-diaza-1,3-diene, RN=CR′CR′=NR) were synthesized as starting materials for the preparation of low valent metal complexes or precatalysts [8]. During cyclic voltammetry studies (CV) on one of these compounds in acetonitrile solution, a steady change in the voltammogram with time was observed. The observation of points of constant potential and current indicate that there is a clean homogeneous chemical conversion of the initial complex into another electroactive species (see Fig. 1a). Repetition of the CV procedure in a cell protected from diffuse daylight led to no such reaction.

Irradiation of complex Ia in acetonitrile solution with light from a halogen lamp leads to a substitution product where formation can be readily monitored by

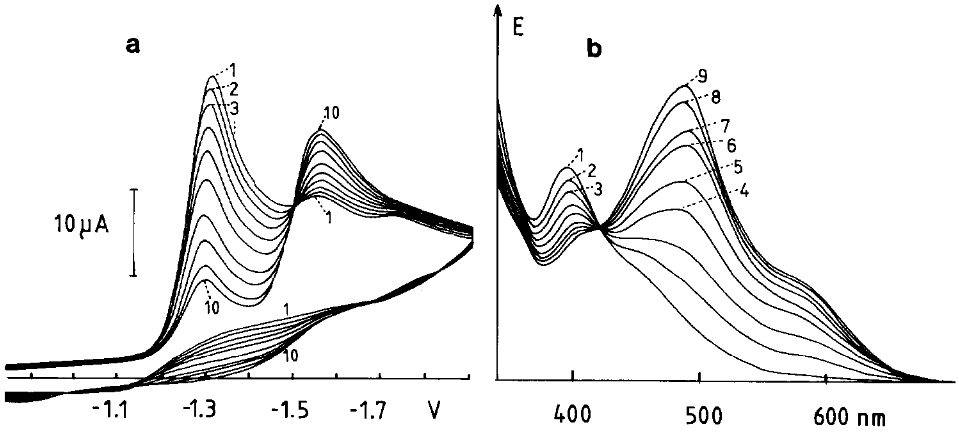
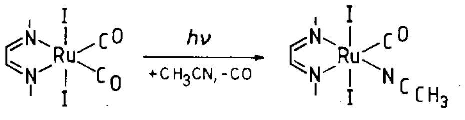


Fig. 1. (a) Cyclic voltammogram of Ia (9.8 mg in 20 ml $CH_3CN/0.1\ M\ Bu_4NClO_4$; 100 mV/s) in diffuse daylight (scans 1–10 after 5, 10, 15, 25, 35, 50, 73, 93, 116 and 136 min); (b) irradiation of Ia in acetonitrile with light $\lambda > 400$ nm (ca. $5 \times 10^{-4}\ M$; scans 1–9 after 0, 0.5, 1, 2, 3, 4.5, 6.5, 30 and 45 min irradiation time).

UV/VIS spectroscopy (Fig. 1b). In spite of the very unfavourable geometry for a photoreaction, irradiation of a sample in an NMR tube (in $CDCl_3/CH_3CN$) also allows NMR monitoring of the reaction (eq. 1).

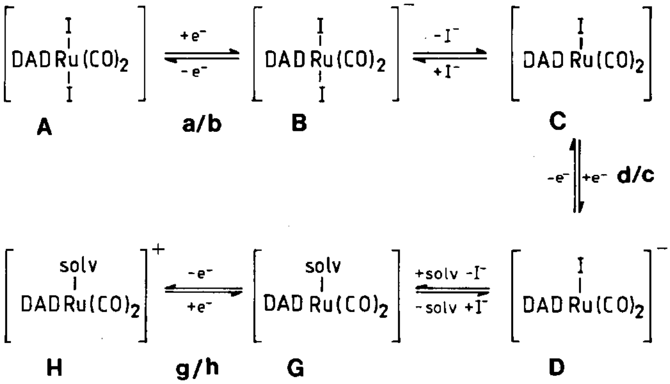


Ia **IIa**

The similarity in the VIS portion of the electronic spectrum of Ia and IIa shows the presence of a chelating DAD ligand [17]. The red shift of the main CT transition reveals that a ligand with a stronger donor and/or poorer acceptor character has entered the coordination sphere. From NMR spectra the stereochemistry of the photoproduct II can be deduced. The nonequivalence of the two halves of the DAD is evident from the doubling of the corresponding signals. An additional signal of coordinated acetonitrile appears at 2.52 ppm. Preparative photochemistry with concentrated solutions gives IIa, which, as expected, exhibits one ν(CO) absorption band at 1975 cm^{-1} in the IR spectrum. The rather poor yield (33%) is probably due to a side reaction, which becomes the predominant reaction in non-coordinating solvents such as dichloromethane. Irradiation of I in this solvent gives a red-brown precipitate of composition $[(DAD)Ru(CO)I_2]_n$ (III). This product is also formed from compound I and trimethylamine oxide in dichloromethane. Irradiation of I with light including wavelengths of < 400 nm leads to a much more complicated outcome, probably including loss of the DAD ligand. Controlled photolysis (> 400 nm) is an interesting means of introducing new ligands into $(DAD)Ru^{II}$ complexes not only in the case of the dicarbonyls I but also in corresponding diolefin complexes [18] and in (DAD)Ru arene complexes [19].

Electrochemistry

Our main objective was to investigate the lower oxidation states of DAD



Scheme 1. The complexes are represented by capital letters. A denotes a complex of type I.

ruthenium complexes, and so the electrochemical behaviour of complexes I was studied by cyclic voltammetry and coulometry. The voltammograms for the glyoxalbis(isopropylimine) complex Ia in acetonitrile are the best for simple analysis. The first irreversible reduction (peak **a**) at −1.36 V (all potentials relative to Ag/0.1 *M* $AgNO_3$ in CH_3CN) is a two-electron reduction, as revealed by a coulometric study at a constant potential of −1.4 V. During the subsequent reoxidation scan, the presence of released iodide is indicated by characteristic peaks (indicated by **i**), representing the redox couples I^-/I_3^- and I_3^-/I_2 [20]. Even with very high sweep rates up to 100 V/s no anodic wave "**b**" corresponding to the initial one-electron transfer is detectable (see Scheme 1).

On the other hand two anodic peaks (**d** and **g**) appear at more positive potentials,

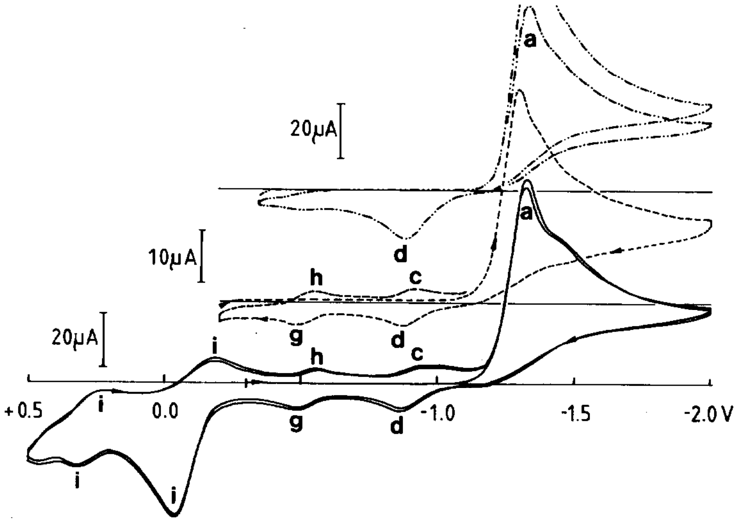


Fig. 2. Cyclic voltammogram of Ia (17.2 mg = 31 μmol; 25 °C; 0.1 *M* Bu_4NClO_4 in CH_3CN, 200 mV/s) ———; repetition of a scan of Ia (arbitrary concentration) between −0.2 and −2 V to avoid the iodine depending redox waves *i* (100 mV/s); ------ repetition (200 mV/s) in the presence of 240 μmol of Bu_4NI rel. to 31 μmol Ia ··—··—··.

and can be attributed to reversible redox couples (**D**/**C** and **G**/**H**). Since peaks **c** and **h** occur only after the first reduction/oxidation cycle, these two complexes must be products of homogeneous chemical reactions following the electrode reaction at -1.36 V (Fig. 2). These two products are of special interest because they provide information about the reactivity of the reduced species **D**. In accord with Scheme 1, we suggest that after the first electron transfer the resulting 19e species **B** rapidly loses one iodo ligand and gives a neutral five-coordinate 17e Ru^I complex **C**. This should be more easily reduced than the starting complex **A** * itself, to give the anionic Ru^0 complex **D**, $[(DAD)Ru(CO)_2I]^-$. This product may then be responsible for the peak pair **d**/**c** corresponding to the reversible couple **D**/**C**. Five-coordinate $(DAD)Ru^0L_3$ complexes are known to be stable when ligands $L_3 =$ arene [5], cycloheptatriene [6], or $(CO)_3$ [21], or when $L_2L' =$ diene and carbon monoxide or diene and triphenylphosphine [6]. An iodide ligand associated with Ru^0 is probably rather labile; associative or dissociative replacement of the iodo ligand by the excess of acetonitrile should occur, and is assumed to be responsible for the peak pair **g**/**h**.

Addition of free iodide does indeed enhance the peak height **d** and reduces or eliminates **g**/**h**. The apparently reversible couple **C**/**D** is affected differently: the reduction peak **c** diminishes with increasing iodide concentration and is virtually absent at a molar ratio of A/I^- equal to 1/10. Since a back reaction of **C** with iodide to the 19e species $[(DAD)Ru(CO)_2I_2]^-$, **B**, is assumed, this behaviour of peak **c** gives an indication of the relative reaction rates (k_{1f}, k_{1b}) and of the equilibrium constant of this first chemical reaction. The fact that the back reaction with iodide is detectable at all can be understood in terms of a reasonable thermodynamic stability of the 19e species **B**. The irreversible peak **a** only provides insight into to the kinetic lability of a 19e complex, the dissociation of which is thermodynamically favoured by the continuous consumption (by reduction) of the 17e correspondent **C**. While peak **a** is representative of an ECE mechanism, peak **d** develops towards that for an ECE type reaction with increasing iodide concentration. Addition of I^- to the five-coordinate oxidation product **C** gives rise to product **B** at a potential much more positive than the peak potential **a**; thus the starting complex **A** is immediately reformed by instantaneous oxidation. In other words, in the presence of added iodide, the peak **d** develops from a (near reversible) one electron transfer to an irreversible two electron transfer. The Ru^0 intermediate $[Ru(DAD)(CO)_2I]^-$ (**D**) should be interceptable by ligands which typically stabilize low oxidation states. This possibility was investigated electrochemically before the preparative work (see below).

Addition of a slight excess of triphenylphosphine to solutions of several complexes of type I showed the typical peak **a** during the first cathodic scan, and, as expected, upon reoxidation a new peak appeared at -0.65 V (for Ia/ $P(C_6H_5)_3$). This potential is more positive than peak **d** (compare Figs. 2 and 3) and slightly less positive than peak **g**, in agreement with the charge and the relative donor properties of iodide, acetonitrile, and triphenylphosphine, respectively. An unexpected feature appeared during the subsequent second cathodic scan: the oxidation of the assumed product of trapping $[(DAD)Ru(CO)_2P(C_6H_5)]$ (IV), is apparently totally irreversi-

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* In Scheme 1 the complexes are represented by capital letters, **A** denotes a complex of type I. The letters **E**, **F**, and **e**, **f** are omitted to avoid confusion with electrochemical symbols.

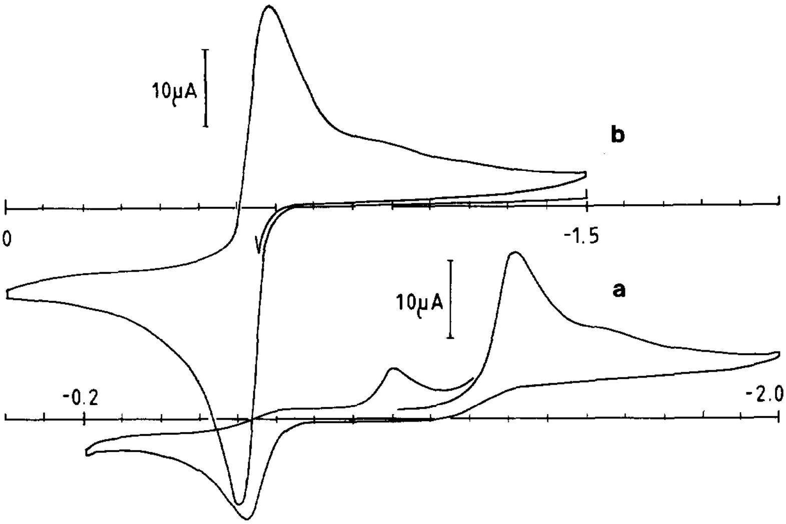


Fig. 3. (a) Cyclic voltammogram of Ia (7.9 mg = 14 μmol) in the presence of triphenylphosphine (6.1 mg = 23 μmol) (20 ml 0.1 *M* Bu_4NClO_4 in CH_3CN at 25° C; 100 mV/s); (b) CV of pure IVa (100 mV/s; 25° C; 0.1 *M* Bu_4NClO_4 in CH_3CN).

ble under the experimental conditions. This is an obvious discrepancy in relation to the (near) reversible situation **d**/**c** and **g**/**h**, with the ligands I^- or CH_3CN instead of $P(C_6H_5)_3$.

Complex IV was synthesized on a preparative scale (see below) and subsequently investigated by CV. Figure 3 shows, in addition to the results of the in situ electrochemical experiment described above, the CV of pure IVa in acetonitrile. Here a quasi-reversible redox couple with E_{pa} −0.59 V and E_{pc} −0.69 V is the salient feature. Addition of small amounts of iodide results in a CV, identical with the complete second scan of the in situ experiment. As discussed above, the very strongly nucleophilic iodide seems to react rapidly with the oxidized complex IV^+. This reaction of a cation with the excess of iodide should be faster than the corresponding reaction involving the neutral 17e iodo complex **C**. The neutral 19e complex $[(DAD)Ru(CO)_2PR_3(I)]$ formed from IV^+ will be further oxidized at the potential at which IV loses its first electron. On the reverse cathodic scan, the resulting cationic 18e -Ru^{II} species is expected to be reduced irreversibly at a potential about 300 mV more positive than that for the starting complex **A**. This is, in fact, the case, as indicated in Fig. 3. The difference of 300 mV is derived by extrapolation from the two reversible couples **d**/**c** and IV/IV^+.

The various DAD complexes I show similar behaviour in cyclic voltammetry. Only complex Id, with a planar, conjugated DAD ligand (glyoxalbis(*p*-tolylimine)), exhibits a reversible **a**/**b** peak. Practically no free iodide is detected during the anodic scan. This changes when the sweep range is extended beyond the second reduction step at −1.75 V, or if the electrode potential is held constant for more than a minute, in the range between the two reduction steps. Obviously, the anionic type **B** complex slowly releases iodide. The further data in Table 1 seem to reflect the different electronic properties of the DAD ligands, although since the reductions are irreversible the peak potentials also depend on kinetic parameters. The presence

Table 1

Peak potentials from cyclic voltammograms of I, IIa and IVa

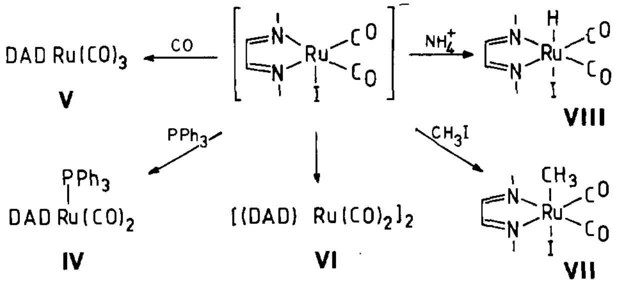
No.	R′	R	Additives	*v*[a]	Peak potentials[b]
Ia	H	i-Pr	–	500	−1.36c, −**0.90a**, −**0.51a**, −**0.58c**, −**0.96c**
			$P(C_6H_5)_3$	200	−1.35c, −0.65a, −1.02c
			Bu_4NI	200	−1.33c, −0.87a
Ib	H	$CH(i\text{-}Pr)_2$	–	200	−1.35c, −0.89a, −0.75a
			$P(C_6H_5)_3$	200	−1.36c, −0.56a, −0.97c
			Bu_4NI	100	−1.33c, −0.91a
Ic	CH_3	i-Pr	–	200	−1.51c, −1.15a
			$P(C_6H_5)_3$	200	−1.54c, −0.69a, −1.19c
			Bu_4NI	200	−1.57c, −1.01a
Id	H	*p*-Tolyl	–	200	−**0.97c**, −1.75c, −**0.90a**
			$P(C_6H_5)_3$	200	−0.99c, −1.71c, −2.11c, −0.91a, −0.67a, −0.70c, −0.87c
			Bu_4NI	200	−**0.95c**, −1.75c, −**0.90a**
Ie	H	2-*m*-Xylyl	–	200	−0.92c, −1.50c, −**0.79a**, −0.65a, −**0.70c**
			$P(C_6H_5)_3$	200	no change
			Bu_4NI	200	−0.89c, −1.50c, −0.68a
If	CH_3	*p*-Tolyl	–	100	−1.23c, −1.04a
			$P(C_6H_5)_3$	100	−1.30c, −0.66a, −0.97c
			Bu_4NI	100	−1.27c, −1.03a
IIa	H	i-Pr	–	200	−1.63c, −1.09a, −1.15c
			$P(C_6H_5)_3$	200	−1.63c, −1.05a, −1.24c
IVa	H	i-Pr	–	200	−**0.59a**, −**0.69c**
			Bu_4NI	200	−0.64a, −1.00c

[a] mV/s. [b] in V vs. Ag/0.1 *M* $AgNO_3$ in CH_3CN. Potentials listed in their order of occurrence during CV; a = anodic, c = cathodic; peaks from reversible couples in bold type.

of methyl substituents (in place of H) on the azomethine carbon atom of the DAD leads to more negative potentials, as earlier demonstrated for the related complexes $[(DAD)Mo(CO)_4]$ [22]. Aromatic N-substituents, whether coplaner or tilted [23], facilitate the reduction. The differences in the CVs of complexes I depend upon the DAD, while in the presence of added triphenylphosphine all the CVs show the three characteristic peaks discussed in detail for Ia. The photochemically prepared complex IIa shows the first reduction at more negative values, as expected for a replacement of carbon monoxide by the stronger donor acetonitrile [22]. The proposed electrochemical reactions described above could be successfully modelled by a simple digital procedure [24], on the basis of a finite differences approximation [25]. Kinetic and thermodynamic parameters derived from high sweep CV and fitting procedures will be discussed elsewhere [24].

Chemical reduction and interception of Ru^0

Electrochemical experiments show that upon reduction the starting diiodo compound I rapidly loses one iodo ligand, while the other is lost only in the presence of better acceptor ligands. It is not known whether the remaining iodo ligand in **D** can dissociate to give a neutral 16e Ru^0 complex or whether a new complex $[(DAD)Ru(CO)_2L]$ is formed via an associative mechanism. The reaction of complexes I with potassium sand (or potassium naphthalenide) in tetrahydrofuran at room temperature depends upon the DAD substituents. With sterically less demanding complexes and in the absence of stabilizing ligands there is generation of a



Scheme 2. Reactions of $[(DAD)Ru(CO)_2I]^-$.

green colour (λ_{max} 645 nm), which slowly turns to a brownish yellow. From these solutions, complexes of composition $[(DAD)Ru(CO)_2]_2$ (V) are obtained. Such complexes have been previously prepared from $Ru_3(CO)_{12}$ by Vrieze's and Van Koten's groups via a substitution reaction [26]. After reduction, complexes with bulky DADs give rise to rather stable black-violet solutions, and no dimers V are formed, in agreement with Vrieze's observation of the dependence of his substitution reaction upon the nature of the DAD. Both the green and the violet solutions are formed from complexes I, which give iodo-containing Ru^0 species after electrochemical reduction. Since the preparative scale reactions involve much more concentrated solutions, it seems quite likely that iodo species are involved here, too. In addition, there may be aggregation via iodo bridges or C=N double bonds (as found for V). The dimers V have not so far been detected in electrochemical experiments. This may be attributable to unfavourable kinetics in dilute electrochemical systems and to the fact that V is irreversibly oxidized at a potential in the region of the iodide oxidation [19].

Addition of triphenylphosphine to the reduced solutions of I leads to isolable complexes IV, which can be readily characterized by spectroscopic methods (IVa, IVc) (Scheme 2, Table 2). Introduction of carbon monoxide into a violet solution (from Ib) gives the red $[(DAD)Ru(CO)_3]$ (VIb), which was prepared previously by a different route [21].

Like other mononuclear $(DAD)Ru^0$ complexes, compounds IV are intensely coloured. The absorption maxima of the CT transition are found at 504 (IVa) and 526 nm (IVc). The IR spectra in hexane exhibit two strong bands below 2000 cm^{-1} due to CO stretching vibrations. The ^1H NMR spectra of IV are rather simple. The isopropyl groups in IVa and IVc show only one doublet for methyl hydrogen atoms. The signals of the azomethine carbon substituents (H or CH_3) and the methine hydrogen of the isopropyl group show a splitting due to coupling to phosphorus. The simplicity of the NMR spectra could be explained in terms of a trigonal bipyramidal structrure of IV with C_{2v} symmetry, i.e. with two axial CO groups, but this is not only the least probable of all eleven possible isomeric structures of a five coordinate complex of type IV, but is not consistent with the $\nu(CO)$ pattern, since this indicates a (OC)–Ru–(CO) angle slightly below 90°. Therefore, the complexes IV must be non-rigid. Low temperature NMR spectra reveal a broadening of the signals, and at 190 K the individual signals are no longer resolved.

The proposed non-rigidity of complexes IV contrasts with recent reports for similar complexes. Thus for [(DAD)Ru(norbornadiene)L] (with L = CO, $P(C_6H_5)_3$),

Table 2

^1H NMR chemical shifts (ppm) and coupling constants (Hz)

No	R′	R	δ and *J* values
IIa	H	i-Pr	8.33 (s, 1H); 8.03 (s, 1H); 4.70 (sept, 2H); 2.52 (s, 3H); 1.68 (d, ^3J 6.9, 6H); 1.56 (d, ^3J 6.6, 6H) [a]
IVa	H	i-Pr	7.37 (d, *J*(H–P) 6.0, 2H); 7.26–7.00 (mult, 15H); 4.41 (d sept, *J*(H–P) 2.0, ^3J 6.5, 2H); 1.15 (d, *J* 12) [b]
IVc	CH_3	i-Pr	7.2–7.0 (15H); 4.40 (br, 2H); 1.84 (d, *J*(P–H) 8.1, 6H); 1.19 (d, ^3J 6.6, 12 H) [b]
VIIa	H	i-Pr	8.16 (s, 2H); 4.49 (sept, 2H); 1.61 (d, ^3J 6.6, 6H); 1.58 (d, ^3J 6.5, 6H); −0.03 (s, CH_3–Ru) [a]
VIIb	H	$CH(i\text{-}Pr)_2$	7.99 (s, 2H); 4.04 (dd, 3*J* 6.0, 2H); 2.71 (m, 2H); 2.29 (m, 2H); 1.14 (d, ^3J 7.0, 6H); 1.07 (d, ^3J 7.0, 6H); 1.04 (d, ^3J 6.8, 6H); 1.03 (d, ^3J 6.8, 6H), −0.02 (s, CH_3–Ru) [a]
VIIe	H	2-*m*-Xylyl	8.30 (s, 2H); 7.2 (m, 6H); 2.64 (s, 3H); 2.32 (s, 3H); 0.33 (s, CH_3–Ru) [a]
VIIIb	H	$CH(i\text{-}Pr)_2$	8.37 (s, 2H); 3.76 (m, 2H); 2.39 (m, 2x2 H); 1.16 (d, ^3J 7.0, 6H)); 1.12 (d, ^3J 7.0); 1.085 (d, ^3J 6.6, 6H); 1.077 (d, ^3J 6.6, 6H); −9.22 (s, Ru–H) [c]

[a] Solvents $CDCl_3$. [b] Solvent C_6D_6. [c] Solvent $(CD_3)_2CO$.

a rigid square pyramidal structure, with L in the apical position, has been unambiguously established [6]. Some similar [(DAD)Fe(diene)CO] complexes are also rigid on the NMR time scale at ambient temperature [27]. [(DAD)Ru(cycloheptatriene)], on the other hand, is fluxional, showing an averaged C_{2v} structure in the NMR [6]. DAD ligands are especially useful for the investigation of stereochemical behaviour, since prochiral and chiral substituents on the nitrogen atoms are readily available [7,28].

As depicted in Scheme 2, the anionic $[(DAD)Ru(CO)_2I]^-$ also reacts with electrophilic reagents. Addition of methyl iodide gives complex VII, $[(DAD)Ru(CO)_2(CH_3)I]$, with the methyl group *trans* to the iodo ligand. The stereochemistry can be deduced directly from the NMR data (Table 2). This reaction requires elevated temperatures. Therefore, complexes Ia and Id cannot be subjected to the corresponding reaction sequence, since the rate of dimerization of their reduced solutions to complexes V is much greater than that of the oxidative addition reaction. The complex VIIa can also be obtained directly from Ia by use of methylmagnesium iodide as alkylating agent. The yield of this direct alkylation is relatively poor owing to a side reaction in which Ia is reduced via the dimethyl compound $[(DAD)Ru(CO)_2(CH_3)_2]$. In the absence of stabilizing ligands (including iodide, since the magnesium diiodide is precipitated), the reduced species decomposes. Nevertheless small quantities of the dimer Va were isolated from the crude reaction product, and reduction must have taken place.

With ammonium hexafluorophosphate in tetrahydrofuran solution at −80 °C the iodo ruthenium(0) intermediate gives the *trans*-hydrido-iodo complex [(DAD)Ru-$(CO_2(H)I]$ (VIII). The hydride signal in the NMR spectrum is found at -9.20 ppm. The stereochemistry of VIII is evident from the number and splitting pattern of the NMR signals from the DAD ligands (Table 2).

Conclusions

It is generally accepted that halides are very poor ligands for metals in low oxidation states and so it is not surprising that they are expelled from the coordination sphere of metal halide complexes during reduction. The interception experiments described above, if they had been undertaken without the prior electrochemical investigations, could have been interpreted as an indirect chemical proof for the existence in solution of a tetra-coordinate Ru^0 species "$[(DAD)Ru(CO)_2]$". Since the second and third row transition metals with d^8 electron configuration and oxidation states II and I prefer the square planar coordination mode, it seems reasonable to argue that zerovalent d^8 metals might also adopt such a geometry, especially if they carry electron-rich ligands. On the other hand, such complexes tend to undergo oxidative addition reactions; this is known for tetraphosphine complexes of ruthenium(0) [29]. $(P)_4RuCl_2$ complexes are extremely difficult to reduce, while the (irreversible) electrochemical reduction of $[(DAD)_2RuX_2]$, i.e. of an $(N)_4RuX_2$ system, is easy in most common solvents used for CV [17a]. In fact, the diazadieneruthenium dicarbonyl moiety is neither rich enough in electrons to exist as a low coordinate species nor sufficiently sterically shielded to prevent (kinetically) the addition of a fifth ligand. The observation, however, of different species in the reduced solutions depending on the steric requirements of the DAD ligand helps in the design of further experiments aimed at stabilizing square planar Ru^0.

In the chemical reactions, on the other hand, complexes of the type $[(DAD)RuL_2(solv)]$ [1,6] or $[(DAD)Ru(CO)_2I]^-$ are interesting and important precursors for the synthesis of new complexes such as IV, VII and VIII, respectively. The hydride VIII is of special interest, since its reduction should give an anionic hydride of Ru^0. The behaviour of complexes I and their reduction and interception products in catalytic reactions are at present under investigation.

Experimental

All reactions and measurements were performed under an inert atmosphere. NMR spectra were recorded on a Bruker WP 80-SYFT or on a Bruker AM 360 instrument. For UV/VIS spectra a Perkin-Elmer Model 554 and for IR spectra a Perkin-Elmer Model 325 spectrometer was used. All solvents were carefully dried. For electrochemical experiments the dry acetonitrile was stored in a brown glass vessel from which it could be distilled into Schlenk vessels immediately before use. Details of the electrochemistry cell have been described earlier [17a,22]. The preparation of complexes I was described previously [8].

Acetonitrile(carbonyl)(glyoxalbis(isopropylimine))-trans-diiodoruthenium (IIa)

A solution of 550 mg (1.0 mmol) of Ia in 40 ml of acetonitrile was irradiated for 4 h with an external halogen lamp. After evaporation of the solvent, the residual material was dissolved in dichloromethane and chromatographed on silica gel. 24% of Ia was recovered. With toluene/CH_2Cl_2 (1/100) as eluent the product was obtained in 33% yield from the second fraction. Analysis: Found: C, 23.66; H, 3.42; N, 6.69. $C_{11}H_{19}I_2N_3ORu$ calcd.: C, 23.43; H, 3.37; N, 7.45%. IR (KBr): ν(CO) 1975 cm^{-1}.

Carbonyl(glyoxalbis(isopropylimine))diiodoruthenium (IIIa)

A solution of 110.9 mg (0.2 mmol) of Ia in 150 ml of dichloromethane was irradiated for 1 h with a high-pressure 125W-Hg-lamp, the radiation being filtered through a 1 *M* sodium nitrite solution. From the opaque solution thus formed a brown solid precipitated out slowly. After 1 day the clear supernatant solution was decanted, and the precipitate washed with dichloromethane and dried in vacuo. Yield: 90%. Analysis: Found: C, 21.06; H, 3.16; N, 5.22. $C_9H_{16}I_2N_2ORu$ calcd.: C, 20.67, H, 3.08; N, 5.35%. IR (KBr): ν(CO) 1946 cm^{-1}.

Carbonyl(glyoxalbis(2,4-dimethyl-3-pentyl-imine))diiodoruthenium (IIIb) was prepared in the same way as IIIa. The precipitation, after 2 h of irradiation, was much slower, and a portion of the product remained in colloidal form. Yield 53%. Analysis: Found: C, 32.21; H, 4.85; N, 4.36. $C_{17}H_{32}I_2N_2ORu$ calcd.: C, 32.14; H, 5.08; N, 4.41%. IR (KBr): ν(CO) 1954, 1941, 1932 cm^{-1}.

Dicarbonyl(glyoxalbis(isopropylimine))triphenylphosphineruthenium (IVa)

A solution of 411.5 mg (0.75 mmol) of Ia in 20 ml of tetrahydrofuran was treated at −70 °C with 20 ml of a 0.069 *M* thf solution of potassium naphthalenide. To the dark reaction mixture was added a solution of 181 mg 0.69 mmol of triphenylphosphine in 5 ml of thf. The mixture was allowed to warm to room temperature and the very air-sensitive red solution was then separated and evaporated. Naphthalene was sublimed under vacuum from the oily product and the residue was then extracted several times with 10 ml portions of hexane. Evaporation of the hexane extracts give the crude product, which was recrystallized from toluene/hexane at −20 °C. After several days a crop of coarse dark crystals (24% yield) was filtered off. The product was characterized by NMR and UV/VIS(hexane) spectroscopy: λ_{max} 504 and 348 nm. IR (hexane): ν(CO) 1976 and 1915 cm^{-1}.

Dicarbonyl(diacetyl(bis(isopropylimine))triphenylphosphine)ruthenium (IVc) was prepared in the same way as IVa in 46% yield. For NMR data see Table 2. UV/VIS (hexane): λ_{max} 526 and 352 nm. IR (hexane): ν(CO) 1969 and 1906 cm^{-1}.

Dicarbonyl(glyoxalbis(isopropylimine)ruthenium dimer (Va)

To a solution of 132.4 mg (0.24 nmol) of Ia in 10 ml of tetrahydrofuran were added 19 mg (0.49 mmol) of potassium sand. The original red colour of the solution darkened and after 2 h had changed to dark green; this colour did not persist, but slowly changed to yellow-brown. The mixture was stirred overnight to ensure complete reduction. After separation of the potassium iodide and evaporation of the solvent, the raw material was purified by column chromatography on silica gel with dichloromethane as eluent. The first yellow fraction contained 25 mg (35%) of the product. Its spectroscopic data are in agreement with literature values [26]. Analysis: Found: C, 40.42; H, 5.19; N, 9.34. $C_{20}H_{32}N_4O_4Ru_2$ calcd.: C, 40.40; H, 5.42; N, 9.42%.

Dicarbonyl(glyoxalbis(p-tolylimine))ruthenium dimer (Vd)

In a procedure similar to that used for the preparation of IV, Id was reduced with potassium naphthalenide in tetrahydrofuran. The crude product, obtained after removal of the potassium iodide by filtration, evaporation, and sublimation of the naphthalene from the residue, was recrystallized from tetrahydrofuran/toluene. The yield from a 0.6 mmol experiment was 48%. NMR spectroscopy and elemental analysis showed the presence of a molecule of tetrahydrofuran in the crystalline product. The spectroscopic data agree with the published values [26]. Analysis: Found: C, 56.24; H, 4.99; N, 6.43. Vd · thf calcd.: C, 55.94; H, 4.69; N, 6.52%.

Diazadiene(dicarbonyl)(iodo)methylruthenium complexes (VII)

These complexes can be prepared either by reaction of I with a methyl Grignard reagent or by addition of methyl iodide to reduced solutions of I.

VIIa: To complex Ia (819 mg; 1.49 mmol) in 40 ml of tetrahydrofuran, 20 ml of a 0.074 *M* ethereal solution of methyl magnesium iodide were added dropwise during 30 min at 0 °C. The solution was filtered and then evaporated, and the residue was transferred to a silica gel column and eluted with dichloromethane. Three fractions were collected. From the first (yellow) fraction the dimer Va was isolated. The second fraction contained 383 mg (0.70 mmol) of Ia. The desired product was contained in the third fraction (194.7 mg, 0.44 mmol). Recrystallization from CH_2Cl_2/hexane gave VIIa as red needles in 30% yield (56% based on Ia consumed). Analysis: Found: C, 30.03; H, 4.29; N, 6.25. $C_{11}H_{19}IN_2O_2Ru$ calcd.: C, 30.08; H, 4.36; N, 6.37%. IR (KBr): ν(CO) 2030 and 1945 cm^{-1}.

VIIb: A solution of 122.6 mg (0.19 mmol) Ib in 10 ml of tetrahydrofuran was stirred overnight with 14 mg (0.37 mmol) potassium sand. After the addition of 0.1 ml of methyl iodide the mixture was refluxed for 2 h. After cooling, filtration and evaporation of the solvent, purification was carried out as for VIIa. The second fraction from the chromatographic separation gave a 57% yield of VIIa. Analysis: Found: C, 40.95; H, 6.25; N, 4.97. $C_{19}H_{35}IN_2O_2Ru$ calcd.: C, 41.38; H, 6.40; N, 5.08%. IR (KBr): ν(CO) 2040 and 1958 cm^{-1}.

VIIe: This sterically hindered complex with glyoxalbis(2,6-dimethylphenylimine) as DAD ligand was prepared in the same way as VIIb. After the first chromatographic purification (silica gel, CH_2Cl_2, fourth fraction) a second was performed with ether as eluant; the product was in the second (greenish) fraction. Analysis: Found: C, 43.02; H, 3.83; N, 4.69. $C_{21}H_{23}IN_2O_2Ru$ calcd.: C, 44.77; H, 4.11; N, 4.97%. IR (KBr): ν(CO) 2045 and 1966 cm^{-1}.

Dicarbonyl(glyoxalbis(2,4-dimethyl-3-pentylimine))hydridoiodoruthenium (VIIIb)

Ib (208.5 mg, 0.31 mmol) were dissolved in 10 ml of tetrahydrofuran and reduced at −70 °C with 10 ml of a 0.062 *M* tetrahydrofuran solution of potassium naphthalenide. To the dark violet reaction mixture was added a solution of 57.1 mg (0.35 mmol) of ammonium hexafluorophosphate in 5 ml of thf. The colour immediately became red-orange. The purification was performed as described for VIIa. A 36.8% yield of orange-yellow crrystals was obtained from the second fraction obtained in the chromatography. The product was characterized by its H NMR spectrum. IR (KBr): ν(CO) 2046 and 1970 cm^{-1}. Analysis: Found: C, 40.66; H, 6.24; N, 5.30. $C_{18}H_{33}IN_2O_2Ru$ calcd.: C, 40.23; H, 6.19; N, 5.21%.

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