Ruthenium Complexes with Diazadienes. 4.[1] Arene Diazadiene Ruthenium(II) Complexes [(η^6-Arene)(RN=CR'—CR'=NR)Ru(L)]$^{n+}$ (n = 1, L = Cl, I, Alkyl; n = 2, L = MeCN, η^2-C$_2$H$_4$) and Arene Diazadiene Ruthenium(0)

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Diazadiene ligands (dad = RN=CR'—CR'=NR) substitute acetonitrile (L) in [(η^6-C$_6$H$_6$)RuL$_2$Cl]$^+$ and give the orange or brown complexes [(η^6-C$_6$H$_6$)Ru(dad)Cl]$^+$ (2) which can be reduced quantitatively to the red complexes (η^6-C$_6$H$_6$)Ru(dad) (5). These Ru(0) half-sandwich compounds undergo oxidative addition with alkyl iodides R''I, to give [(η^6-C$_6$H$_6$)Ru(dad)(σ-R'')]$^+$. Their rate of formation strongly depends on steric factors. A σ-ethyl complex (R'' = Et) reacts further with trityl tetrafluoroborate with hydride abstraction to give the [(η^6-C$_6$H$_6$)(η^2-C$_2$H$_4$)Ru(dad)]$^{2+}$ cation. A similar series of complexes is obtained with the asymmetrical arene 1,2-diethyl-4-methylbenzene, introducing a chiral arene ruthenium fragment. ^{1}H NMR spectra are discussed with respect to symmetry, diastereotopy, and chirality as well as conformational barriers and related steric problems. The η^6-arene and the dad ligands are close enough to each other so that the arene can determine the conformation of the dad N substituents; vice versa, larger N substituents contribute to the lability of the η^6-arene. Cyclovoltammetric studies show the enhanced arene lability on oxidation of 2; the likewise irreversible reduction proceeds, in agreement with preparative reactions, with loss of Cl$^-$ and formation of the Ru(0) complexes 5. According to electron spectroscopic data dad ligands display their special properties more clearly in complexes of low formal oxidation state. The Ru → dad CT absorptions are not very characteristic in the Ru(II) complexes 2 as compared to (dad)Ru^{II} systems with stronger donor ligands. In the Ru(0) case the increase in absorption intensity, the absence of solvato-chromism, and the dependence on substituents indicate, together with electrochemical results, the increasing π → π* character of the main absorption band, which is related to strong ground-state back-bonding. The bonding is discussed in comparison to other half-sandwich complexes.

Introduction

Complexes of transition metals in low oxidation states with one *diazadiene* (dad) ligand RN=CR'—CR'=NR (1) can be interesting precursors for various highly selective and specific homogeneous catalytic reactions, as it was shown for chromium,[2] nickel,[3] iron,[4-9] or rhodium.[10] The advantage of dad ligands as compared to 2,2'-bipyridine in general[1] and with respect to back-bonding[11] has been pointed out. Besides their behavior as chelating ligands it was with ruthenium that the greatest variability of other dad bonding modes was established.[12] The interesting

catalytic properties of the (dad)Fe^0 fragment[8,9] encouraged us to attempt the synthesis of mono(diazadiene)ruthenium complexes with further, possibly labile ligands. Simple η^6-arene chloro complexes of Ru(II) are well-known,[13] substitution reactions with retention of the arene have been reported,[14,15] and (η^6-arene)Ru^{0}L$_2$ complexes with donor ligands L = PR$_3$ have been characterized.[16,17] Half-sandwich complexes of the type (arene)ML$_2$ have recently attracted much interest as metal bases,[18] and theoretical descriptions based on extended Hückel calculations have been useful in understanding structures and reactions.[19] The synthesis of (bpy)(η^6-toluene)Fe^0 by means of metal atom techniques[20] was another encouraging hint that η^6-arene complexes of Ru should be stable molecules accessible via classical chemical reactions.

Results and Discussion

Preparation and Reactions. The dinuclear benzene

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ruthenium complex $[Ru(C_6H_6)Cl_2]_2$,[13] which reacts with various nucleophiles L to give complexes $Ru(C_6H_6)Cl_2L$[14] or with excess L or chelating ligands L–L to give ionic complexes $[Ru(C_6H_6)(L-L)Cl]^+$,[15,21] did not yield pure products in the thermal reaction with 1,4-diaza-1,3-dienes (dad), RN=CR'—CR'=NR. Therefore we used silver tetrafluoroborate in acetonitrile to prepare the more reactive $[Ru(C_6H_6)(CH_3CN)_2Cl]^+BF_4^-$. After filtration of the silver chloride precipitate, the orange yellow solutions react in boiling acetonitrile with equimolar amounts of dad 1a–k to give the complexes $[Ru(C_6H_6)(dad)Cl]BF_4$ (2a–k).
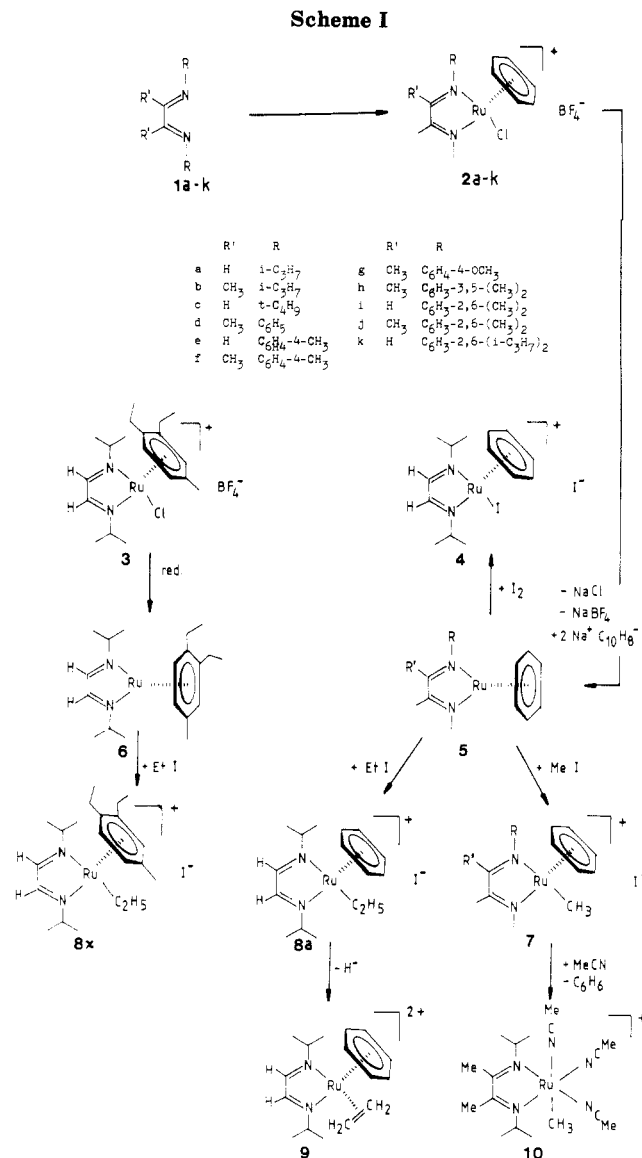
When the synthesis of the arene complex starts from substituted cyclohexadienes instead of cyclohexadiene itself, asymmetric arene ruthenium complexes are accessible. Thus 1,2-diethyl-4-methyl-1,3-cyclohexadiene, readily synthesized by iron(0)-catalyzed Diels–Alder reaction of 3-hexyne and isoprene,[7] gives, in a manner completely analogous to the synthesis of 2 the 1,2-diethyl-4-methylbenzene ruthenium complex 3, containing a dad ligand with prochiral substituents. Finally an iodo iodide complex, $[Ru(C_6H_6)(dad)I]I$ (4), is obtained by the iodine oxidation of the ruthenium(0) complexes, described in Scheme I.

Complexes 2 and complex 3 can be reduced by sodium naphthalene in THF at ambient temperature to the red, oxygen-sensitive and alkane-soluble complexes (arene)-Ru(dad) (5 and 6). As the radical anions $dad^{\bullet-}$ $(1^{\bullet-})$[22,23] are much more nucleophilic, the synthesis of complex 5 can also be achieved directly from $[(C_6H_6)RuCl_2]_2$, dad 1, and sodium, although the total yield of pure 5 is better in the stepwise synthesis via 2. In contrast to the thermally labile phosphine complexes $Ru(C_6H_6)(PR_3)_2$,[16] complexes 5 and 6 melt without decomposition or sublime in vacuo, withstanding temperatures up to 200 °C.

Like many other $M(C_6H_6)L_2$ complexes,[18] the ruthenium(0) compounds should behave as metal bases. Because of stereochemical considerations most reactions of 5 with electrophiles were carried out with the N-isopropyl-substituted diazabutadiene 1a. 5 does not react with ammonium hexafluorophosphate; with anhydrous tetrafluoroboric acid in ether or gaseous HCl in hexane yellow oils are formed, which do not show the expected Ru–H vibrations or NMR signals. The slow reaction of methyl iodide with 5 in hexane yields yellow to brown crystalline σ-alkyl compounds 7, in which the iodide is easily exchanged by the PF_6^- or BF_4^- anions. The addition of ethyl iodide to 5 in hexane is even slower, yielding the σ-ethyl complex 8a, which is quite stable. Addition of trityl-tetrafluoroborate to 8a gives the η^2-ethylene complex cation $[(C_6H_6)Ru(dad)(C_2H_4)]^{2+}$ (9) by hydride abstraction.

The stability of the diazadiene ruthenium σ-alkyl compounds depends on the steric requirements of both the dad and the alkyl group. 5a is stable in dichloromethane, acetonitrile, and other nucleophilic solvents; 5b is stable in dichloromethane, but in acetonitrile the η^6-benzene is substituted completely within 3 days at room temperature by three solvent molecules to give 10. The N-tert-butyl complex 5c still reacts with methyl iodide, but decomposition of the resulting complex 7c cannot be suppressed. The σ-ethyl compound 8a, with the same dad as in 7a, reacts slowly with acetonitrile with η^6-benzene substitution.

Reaction of 5a with allyl chloride in hexane is very fast, but the yellow intermediate of type 7 (σ-allyl) decomposes

Scheme I

	R'	R		R'	R
a	H	i-C_3H_7	g	CH_3	C_6H_4-4-OCH_3
b	CH_3	i-C_3H_7	h	CH_3	C_6H_3-3,5-$(CH_3)_2$
c	H	t-C_4H_9	i	H	C_6H_3-2,6-$(CH_3)_2$
d	CH_3	C_6H_5	j	CH_3	C_6H_3-2,6-$(CH_3)_2$
e	H	C_6H_4-4-CH_3	k	H	C_6H_3-2,6-(i-$C_3H_7)_2$
f	CH_3	C_6H_4-4-CH_3			

very rapidly. No formation of an iodo complex of type 4 could be detected during the reactions of 5 with R''I, in contrast to the results obtained with $(\eta^6-C_6H_6)Ru(PMe_3)_2$.[16]

In principle, complexes 7 or 8 should also be obtainable by nucleophilic alkylation of 2 with Grignard reagents. Reaction of 2a with stoichiometric amounts of MeMgI in THF or diethyl ether gave a mixture of 45% of the starting material 2a, 45% of the iodo cation of type 4, and only 10% of 7a, although workup was performed in dichloromethane, a solvent, in which the alkylated cations 7 are stable. There must be other ways for halide exchange to occur than the ones postulated for $(alkyl)(Cp)RuL_2$.[24,25]

^{1}H NMR Spectroscopy and Structure. The stereochemistry of the described benzene complexes and some important conformational barriers can be deduced from the ^{1}H NMR data. Complexes 2 can be regarded as derived from octahedral coordination; a mirror plane bisecting the dad ligand is the only symmetry element. This is clearly visible from the ^{1}H NMR data of 2a,b and 4 with prochiral N substituents; different signals for diastereotopic groups are observed. In 2k, with o,o'-diisopropylphenyl N substituents on the dad, four CH_3 doublets are separated (see Table I). The N substitutent does not

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Table I. ^{1}H NMR Data of $[(\eta^6\text{-}C_6H_6)(dad)RuX]^+Y^-$ Complexes 2a–k and 4 in CD_3CN^a

				δ and J values				
compd	R′	R	C_6H_6	R′		R		
2a	H	*i*-Pr	5.97	8.17	4.86 (H$_\alpha$)		1.54 (H$_\beta$)/1.44 (H$_{\beta'}$)	$J_{\alpha\beta}$ = 6.6 Hz
4	H	*i*-Pr	6.07	8.11	4.78 (H$_\alpha$)		1.57 (H$_\beta$)/1.51 (H$_{\beta'}$)	$J_{\alpha\beta}$ = 6.6 Hz
2b	Me	*i*-Pr	5.94	2.41	4.92 (H$_\alpha$)		1.64 (H$_\beta$)/1.46 (H$_{\beta'}$)	$J_{\alpha\beta}$ = 6.9 Hz
2c	H	*t*-Bu	6.10	8.21	1.61			
2d	Me	Ph	5.29	2.26	7.5 (b)			
2e	H	*p*-MePh	5.62	8.28	7.68	7.40		$J_{o,m}$ = 8.5 Hz
2f	Me	*p*-MePh	5.28	2.24	7.3 (b)		2.45 (*p*-Me)	
2g	Me	*p*-OMePh	5.31	2.26	7.41	7.11	3.88 (*p*-OMe)	$J_{o,m}$ = 9 Hz
2h	Me	$m,m'\text{-}(Me)_2Ph^b$	5.33	2.26	7.07 (H$_o$)	7.16 (H$_p$)	2.43 (*m*-Me)	
2i	H	$o,o'\text{-}(Me)_2Ph$	5.54	8.36	7.31		2.45/2.22 (*o,o′*-Me)	
2j	Me	$o,o'\text{-}(Me)_2Ph$	5.36	2.16	7.39		2.41/2.16 (*o,o′*-Me)	
2k	H	$o,o'\text{-}(i\text{-}Pr)_2Ph$	5.54	8.43	7.49	3.77	1.31/1.08 (*o-i*-Pr)	
						2.62	1.49/1.18(*o′-i*-Pr)	

^{a} Chemical shift values are reported in ppm from SiMe$_4$, measured at 30 °C. ^{b} Measured at 72 °C.

Table II. ^{1}H NMR Data of $(\eta^6\text{-}1,2\text{-}(Et)_2\text{-}4\text{-}Me\text{-}C_6H_3)Ru(i\text{-}PrN{=}CHCH{=}N\text{-}i\text{-}Pr)$ Complexes $3,^a$ $6,^b$ and $8x^c$

compd		δ and J values
3	η^6-arene	5.63 (s, H3); 5.75 (H5); 5.71 (H6, $J_{5,6}$ = 5.8 Hz); 2.24 (s, Me); 1.34, 1.31 (t, Me, J_{vic} = 7.5 Hz); 2.69, 2.54/2.74, 2.58 (mult, J_{gem} = 15.3 Hz)
	dad	8.26, 8.25 (s, HC=); 4.81, 4.75 (sept, CHMe$_2$, J_{vic} = 6.6 Hz); 1.66, 1.65, 1.49, 1.48 (d, Me)
6	η^6-arene	4.34 (s, H3); 5.01 (H5); 4.39 (H6, $J_{5,6}$ = 5.4 Hz); 2.06 (s, Me); 1.11, 1.09, (t, Me, J_{vic} = 7.4 Hz); 2.50, 2.49, 2.31, 2.30 (mult, CH_2Me, J_{gem} = 14.6 Hz)
	dad	7.04 (s, HC=); 4.53 (sept, CHMe$_2$, J_{vic} = 6.8 Hz); 1.44, 1.42 (d, Me)
8x	η^6-arene	5.40 (d, H3, $J_{3,5}$ = 0.9 Hz); 5.59 (dd, H5); 5.64 (d, H6, $J_{5,6}$ = 5.4 Hz); 2.27 (s, CH$_3$); 1.15, 1.21 (t, CH_3CH$_2$, J_{vic} = 7.5 Hz); 2.38, 2.59 (2dq, CHH′CH$_3$, J_{gem} = 13.7 Hz); 2.28, 2.58 (2dq, CHH′CH$_3$, J_{gem} = 14.6 Hz)
	dad	8.30 (s, HC=, J_{vic} = 0.5 Hz); 4.32 (sept, CHMe$_2$, J_{vic} = 6.5 Hz); 1.32, 1.31 (d, (CH$_3$)$_2$CH); 4.38 (sept, CHMe$_2$, J_{vic} = 6.5 Hz); 1.48, 1.46 (d, (CH_3)$_2$CH)
	σ-C$_2$H$_5$	0.75 (dq, CHH′CH$_3$, J_{vic} = 7.1 Hz); 0.69 (dq, CHH′CH$_3$, J_{vic} = 7.6 Hz, J_{gem} = 9.5 Hz); 1.14 (t, CH$_3$)

^{a} In CD$_2$Cl$_2$, 270 MHz, 30 °C. ^{b} In C$_6$D$_6$, 400 MHz, 25 °C. ^{c} In CD$_2$Cl$_2$, 360 MHz, 26 °C; all δ values in ppm from SiMe$_4$.

Table III. ^{1}H NMR Data of $(\eta^6\text{-}C_6H_6)Ru^0(dad)$ Complexes 5

compd			δ values^a					
no.	R′	R	η^6-C$_6$H$_6$	R′		R	J values	solv
5a	H	*i*-Pr	4.84	7.03	4.39 (H$_\alpha$)	1.40 (H$_\beta$)	J_{vic} = 6.7 Hz	C$_6$D$_6$
5c	H	*t*-Bu	5.43	7.00	1.62			
5e	H	*p*-MePh	5.07	6.95	7.32, 7.15		$J_{o,m}$ = 8.5 Hz	CD$_2$Cl$_2$
5f	Me	*p*-MePh	4.59	1.80	7.18, 6.97		$J_{o,m}$ = 8.2 Hz	C$_6$D$_6$
					2.22 (s, *p*-Me)			
5b (77 °C)	Me	*i*-Pr	4.98	1.74	4.56 (H$_\alpha$)	1.35 (H$_\beta$)	J_{vic} = 6.9 Hz	C$_6$D$_5$CD$_3$
5b (−33 °C)		AA^b 55%	5.09	1.78	4.29	1.30	J_{vic} = 6.7 Hz	
		AB^b 40%	4.90	1.86/	4.7–5.1	1.38		
				1.73		1.30		
		BB^b 5%	4.74	1.83	4.20	1.38		

^{a} All δ values are reported in ppm from SiMe$_4$. ^{b} See Figure 1.

rotate around the N-aryl bond at room temperature on the NMR time scale. This is also evident from the two o-CH$_3$ signals in **2i** and **2j**. The $\delta(C_6H_6)$ value depends on the dad conformation. In complexes with N-alkyl dad, **2a–c**, and **4**, it is around 6 ppm; in glyoxal-derived N aromatic dad (R′ = H) 5.6 ppm is a typical value, while for biacetyl derived dad, in which the aromatic N substituents are a priori tilted out of the dad coordination plane, 5.3 ppm is a typical $\delta(C_6H_6)$ value. These differences could reflect the average position of η^6-benzene protons relative to the shielding or deshielding areas of the aromatic N substituents in combination with the sterically allowed approach of the arene. Strong NMR effects in rigidly packed coordination spheres of dad complexes are known.[1,6] The rather large difference in δ of 1.15 ppm for the two methine protons of the *i*-Pr groups in **2k**, on the other hand, indicates their different position with respect to the deshielding area of the η^6-benzene ring.

As in other complexes of biacetyl bis(arylimines),[1] the N-aryl rotation is hindered. Variable-temperature spectra allow the estimation of the barriers of rotation ($\Delta G^{\ddagger}$ (**2g**) = 53 kJ/mol and $\Delta G^{\ddagger}$ (**2h**) = 63 kJ/mol), which are appreciably lower than in complexes (dad)$_2$RuX$_2$.[1] Rotational

barriers in complexes **2** are therefore more intra- than interligand in character.

The C_s symmetry of complexes **2**, which is evident from all NMR data discussed so far, can be eliminated by introducing an asymmetrically substituted arene, as in **3**. All dad signals in **3** are doubled with respect to **2a**. This excludes a rotation of the dad ligand, by which the two ligand halves would be interchanged. The chirality of the complex resides, of course, in the asymmetric arene–Ru fragment; the prochiral methylene hydrogens of the two Et groups give rise to a complex pattern, which could be calculated by assuming that $J_{gem} \approx 2J_{vic}$ (see Table II). For the ruthenium(0) complexes **5** the ^{1}H NMR spectra are also useful in establishing structural features. The data are collected in Table III. Just as for other (arene)RuL$_2$ complexes,[16,26] the η^6-C$_6$H$_6$ proton NMR signal is observed at higher field than with [(arene)RuL$_2$X]$^+$ analogues. The complexes (arene)FeL$_2$ (L = (PR$_3$)$_2$ or dienes) have also been prepared by metal atom techniques,[27] but there is

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Table IV. ¹H NMR Data of (σ-Alkyl)ruthenium Complexes 7 and 8 and Reaction Products 9 and 10

compd			δ and J values						
no.	R'	R	C₆H₆	R'	σ-alk	R			solv
7a	H	i-Pr	5.95	8.27	0.42	4.55 (Hₐ)	1.44/1.30 (Hᵦ)	J = 6.6 Hz	CD₂Cl₂
7b	Me	i-Pr	5.82	2.40	0.49	4.57 (Hₐ)	1.56/1.43 (Hᵦ)	J = 6.7 Hz	CD₂Cl₂
7e	H	p-MePH	5.61	8.26	0.78	7.34 (H$_{arom}$)	2.43 (p-Me)		CD₃CN
7f	Me	p-MePh −33 °C	5.14	2.19	0.75	7.30 (4 H), 2.39 (p-Me)	7.25/6.84 (2 × 2 H, d)		CD₂Cl₂
7f	+37 °C		5.18	2.26	0.81	6.8–7.5 (H$_{arom}$, br)			
						2.43 (p-Me)			
8a	H	i-Pr	5.98	8.34	0.87 (Hₐ) 1.56 (Hᵦ)	4.57 (Hₐ)	1.56/1.43 (Hᵦ)	J = 6.6 Hz	CD₂Cl₂
9	H	i-Pr	6.62	8.10	4.36ᵇ	4.80 (Hₐ)	1.57/1.46 (Hᵦ)		CD₃CN
10	Me	i-Pr	...	2.18	−0.66	4.54 (Hₐ)	1.51/1.34 (Hᵦ)ᶜ		CD₃CN

ᵃ All δ values are reported in ppm from SiMe₄, measurement at 30 °C unless otherwise stated. ᵇ η²-C₂H₄. ᶜ Ru-bonded CD₂HCN (from solvent) not detected.

only one example with a chelating N ligand, (η⁶-MeC₆H₅)Fe(bpy),[20] which can be compared (δ(H$_{arom}$) 5.0–5.4 in C₆D₆).

The time-averaged structure contains an N,N′ σ-chelating dad ligand in an arrangement perpendicular to the η⁶-benzene plane. Although numerous π-bonding modes are known for (dad)Ru carbonyl complexes,[12] these can be excluded, because any such structure would make the Me groups in **5a** diastereotopic and thus magnetically inequivalent. Low-temperature spectra (C₆D₅CD₃, −80 °C) do not show further splittings or unusual shifts for **5a,c**.

The fast rotation of the benzene ring, which always shows a sharp singlet signal, does not necessarily follow from the spectra of **5**. The introduction of chirality can be used to show that full (360°) rotations, even of the sterically more demanding arenes, occur rapidly: in **6**, with the arene η⁶-1,2-(Et)₂-4-Me-C₆H₃, the prochiral Me group in the N substituents are now diastereotopic, while the N substitutents as a whole or the azomethine H atoms R′ are still equivalent (see Table II).

Chirality in a molecule has no effect on groups interchanged by real rotational movements, but chirality, of course, helps to discriminate between groups interchangeable only by virtual total or local rotational symmetry. The chiral complexes **3** and **6** are good examples for this trivial, but sometimes overlooked statement.

The δ values for the imine protons (R′ = H) are shifted downfield in **2** and upfield in complexes **5** relative to the free ligand. This indicates substantial electron transfer from the Ru(0) to the dad π* level (see below). An unusual feature shows up in the low-temperature spectrum of **5b** with a biacetyl bis(isopropylimine) ligand, **1b**. It consists of three superimposed spectra of conformers, which collapse to the simple high-temperature spectrum. The preferred N-i-Pr conformation of the free ligand **1b**[22,28] and of the complexed ligand in **5b** is probably the one shown on the left side of Figure 1. The crowding of methyl groups in the other probable conformation is accompanied by a reduction in interaction with the η⁶-benzene ring (conformation B). The conformer with two i-Pr groups in position A is the preponderant one (~55% at −33 °C). The asymmetrical conformer with one i-Pr group with A and the other with B conformation accounts for 40% (by NMR integration) of the mixture, while only 5% have both i-Pr groups in the unfavorable conformation B. The two inequivalent halves of the dad ligand in the AB conformer show up in a doubled set of dad ligand signals of half the relative intensity of the correlated one benzene signal for this moiety. A similar phenomenon was observed with
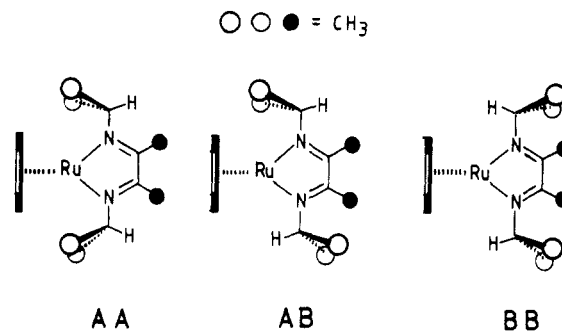
○ ○ ● = CH₃

Figure 1. Probable low-temperature conformers (−33 °C) of **5b**.

CpCo(dad) (dad = **1b**);[29] here the unsymmetrical conformer is the preponderant one. It is not unlikely that the aromatic rings in both the Co and Ru AB conformers are no longer perpendicular to the dad chelate plane. The conformation B—as a corollary—means that it might be possible to accommodate a t-Bu group at this sp² N atom, although all attempts to condense biacetyl with t-Bu-NH₂, or other aliphatic (R′ ≠ H) 1,2-dicarbonyl compounds with tert-alkylamines, have failed so far.

The electrophilic addition of alkyl halides to **5**, which gives **7** or **8**, should lead back to the same symmetry as in **2**. Multiplicity and number of resonances are indeed the same as in the chloro complexes **2**, with addition of the σ-alkyl resonances (see Table IV). The extremely slow addition of EtI to **6** gives the chiral **8x**, in which all three CH₂ groups show the complex quadrupled AB pattern of a diastereotopic pair of H atoms coupled to a Me group (see Table II). The η²-ethylene complex **9** from the hydride abstraction of **8a** again has the same symmetry as **2**. The two Me groups of one i-Pr substituent are still diastereotopic; the sharp ethylene singlet at 4.38 ppm, a value similar to that in [Rh(η⁵-C₅H₅)(PMe₃)₂(η²-C₂H₄)]²⁺,[30] indicates fast rotation, which eliminates the diastereotopicity of geminal or cis-vicinal ethylene protons in rigid hypothetical configurations of Cₛ symmetry. The π-benzene resonance approaches the value of free benzene, which is reasonable for [Ru]²⁺ complexes.

The nucleophilic substitution **7 → 10** of the arene in Ru half-sandwich compounds is not unprecedented.[17,31] The NMR indicates that a facial (MeCN)₃Ru complex **10** is formed. Again the value of prochiral substituents (in this example the i-Pr group of **1b**) for structure determinations

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Table V. Electronic Spectral Data of 2, 3, 4 (in MeCN), 5, 6, 7, and 8 (in CH₂Cl₂)

compd	λ, nm (ε, M⁻¹ cm⁻¹, or E, aritrary units[a])			compd	λ, nm (ε, M⁻¹ cm⁻¹, or E)		compd	λ, nm (ε, M⁻¹ cm⁻¹, or E)	
2a	492[b] (320)	418 (2100)	358 (1700)	5a	488[b] (1200)	412 (16000)	7a	428 (7600)	300 sh
3	...	425 (1.0)	365 (0.64)	6	495 (0.11)	419 (1.0)	8a	434 (1.0)	340 (0.14)
4	460 (0.2)		355 (1.0)						
2b	465 (560)	409 (1700)	338 (2500)	5b	512 (0.11)	434 (1.0)	6b	428 (6300)	340 sh
2c	490 (420)	423 (1400)	367 (1700)	5c	510 (0.12)	432 (1.0)			
2d	520 (240)	406 (2800)	344[c] (3500)						
2e	545 (1100)	448 (3200)	374 (12000)	5e	512 (0.12)	433 (1.0)	7e	458 (0.62)	358 (1.0)
2f	510 (290)	40 (3100)	343 (4900)	5f	510 (0.10)	431 (1.0)	7f	436 (1.0)	326 (0.46)
2g	520 (510)	410 (4200)	384[c] (5400)						
2h	510 (120)	400 (1700)	342 (2600)						
2j	520 (250)	455 (1600)	405[c] (3100)						
2k	600 (80)	485 (1300)	430[c] (2400)						

[a] Values with decimal numbers relative to strongest absorption with $E = 1.0$. [b] All values in this column refer to shoulders. [c] Further maximum at 340–370 nm (ε 2000–5000).

becomes evident. The σ-Me signal, now at –0.66 ppm, is shifted by almost 1.5 ppm upfield with respect to the C₆H₆ complex 7b, while there is no special influence on the dad resonances (Table IV). The much greater electron density in 10 relative to 7b, responsible for this δ difference, is paralleled in the differences in the oxidation potentials of analogous chloro complexes 2 and 12 (see below).

Electronic Spectra, Electrochemical Behavior, and Bonding. A thorough discussion of the electronic spectra of complexes 2 with their low symmetry is difficult. As shown earlier, closed-shell complexes of diazadienes with metals in low formal oxidation states show strong MLCT absorption bands,[32] which dominate the visible part of the electronic spectrum. This is also true for bpy and dad complexes of metals in "normal" oxidation states, if these can be considered to be rich in electrons. [(bpy)₃Ru]²⁺,[33] [(dad)₃Ru]²⁺,[1,34] *cis*- or *trans*-(bpy)₂RuX₂ and (dad)₂RuX₂,[1,35,36] or (dad)Ru(PhCN)₂X₂[37] are examples thereof. CT transitions Ru → C₆H₆ are found around 250 nm in [Ru(C₆H₆)Cl₂]₂.[38] Therefore, the bands with ε values of >2000 L·mol⁻¹·cm⁻¹ above 400 nm must be attributed to transitions from the metal into the π* dad orbital. As in (dad)M(CO)₄ complexes (M = Cr, Mo, W)[32,39] with the same ligands, 2e with a coplanar *N*-aryl substituent shows a bathochromic shift relative to 2f and the N-alkylated dad complexes (Table V).

In both the Ru(II) complex 3 and the Ru(0) complex 6, with the 1,2,4-substituted η⁶-arene, the main CT transition is slightly shifted to longer wavelengths (Table V). This, too, is in agreement with a Ru → π*(dad) character for the main absorption band, since the substituted arene in comparison to benzene should raise the energy of the metal d electrons. Reoxidation of 5 to 7 or 8 leads to σ-alkyl complexes, which show a bathochromic shift as compared to the isoelectronic chloro compounds 2 (Figure 2). LF bands of 7 are expected at higher energies than those of 2. This finding also supports the assignment of strong band in the visible as MLCT. The influence of the dad N substituents is characteristic as well (Table V). In
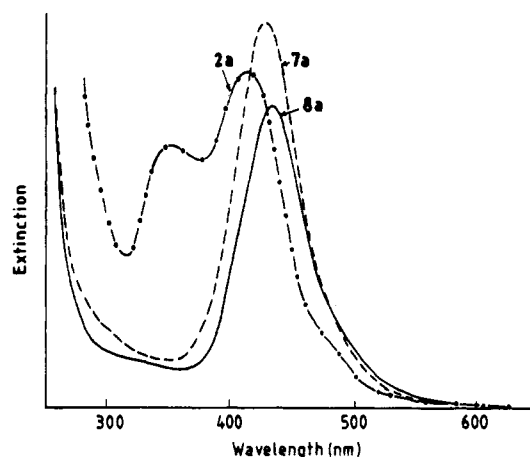

Figure 2. Electronic absorption spectra of 2a, 7a, and 8a in acetonitrile.
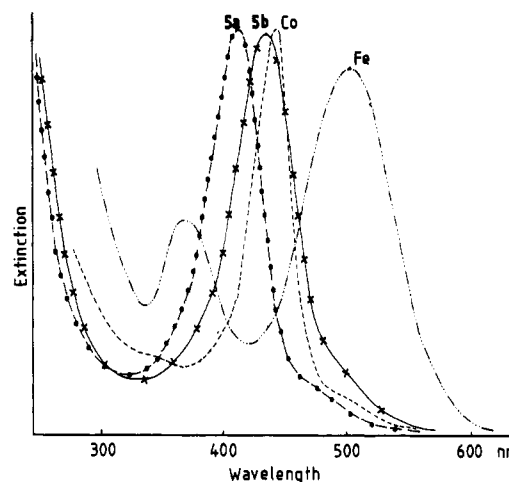

Figure 3. Electronic absorption spectra of 5a and 5b in comparison to five-coordinate analogues (η⁵-C₅H₅)Co(dad) (Co) and (dad)Fe(CO)₃ (Fe), both with dad = 1a (in *n*-hexane).

Figure 2 the spectra of octahedral Ru(II) complexes are shown for comparison. The band at 350 nm in the spectrum of 2a shows strong intensity changes, when the halo ligand or the dad is changed. We could not assign this band.

Unfortunately the electronic spectra of six-coordinate 2 cannot be compared with five-coordinate Ru(0) complexes 5. The electronic spectra of the latter resemble those of (dad)Co(η⁵-C₅H₅)[29] or (dad)Fe(CO)₃.[40] While

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(33) Kober, E. M. Meyer, T. J. *Inorg. Chem.* 1982, *21*, 3967 and references cited therein.

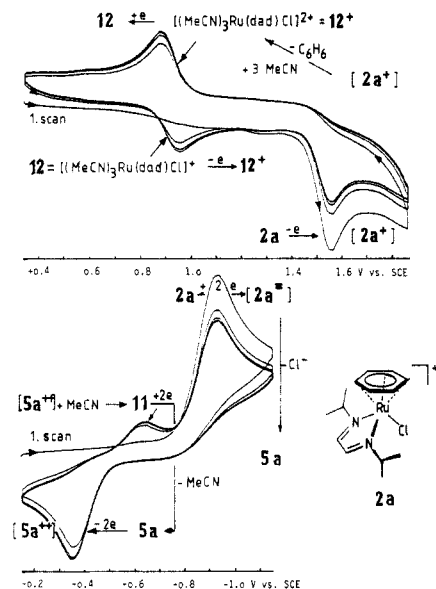(34) Krug, W. P.; Demas, N. J. *J. Am. Chem. Soc.* 1979, *101*, 4394.

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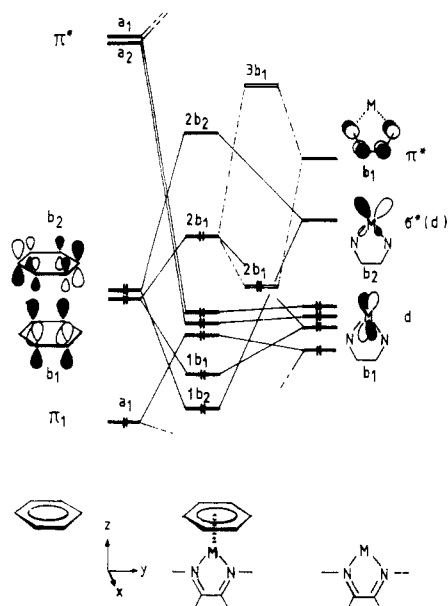
(40) tom Dieck, H.; Orlopp, A. *Angew. Chem.* 1975, *87*, 246; *Angew. Chem., Int. Ed. Engl.* 1975, *14*, 251.

Figure 4. Cyclic voltammograms of the oxidation (above) and the reduction (below) of **2a** in acetonitrile.

Figure 5. MO diagram for $(\eta^6\text{-arene})M(dad)$ (5). The HOMO $2b_1$ is π-antibonding with respect to the M/arene interaction. The intervention of the low-lying b_1 dad π^* orbital stabilizes $2b_1$ $(-\cdot-)$. An electronic transition $2b_1 \to 3b_1$ (z-polarized "CT" transition) reduces the M/arene antibonding and enhances the M/dad antibonding (see text).

most of the Ru(0) complexes show one intense band near 430 nm, accompanied by a long wavelength shoulder, and resemble thus very much the Co complex, also shown in Figure 3, the Fe(CO)₃ complex shows the corresponding MLCT band at much lower energies. This reflects the different electronic properties of the aromatic ligand as compared to three CO groups. The MO discussion (see below) will show that the occupied π orbitals of the arene influence the frontier orbitals appreciably, while in carbonyl complexes the empty π^* orbitals play an important role.

The electrochemical reduction of **2** in acetonitrile is irreversible. The chemical reduction, as described above, gives the Ru(0) complexes **5**. If one compares **2** with the equally octahedral complexes M(CO)₃(dad)L (M = Cr, Mo, W; L = CO, MeCN),[41] one expects that the ligand with the lowest back-bonding capacity is expelled. In agreement with the chemical reduction, the chloro ligand is lost. The two-electron reduction leads to (C₆H₆)Ru(dad) (5). Its oxidation on the reverse scan in acetonitrile must again be irreversible, since a five-coordinate Ru(II) species would immediately take up a sixth ligand, acetonitrile. An immediate second reduction scan reveals the presence of a new, electrochemically formed product, which itself is reduced irreversibly at a more positive potential (~0.5 V) relative to **2**. The newly formed product must be [(η⁶-C₆H₆)Ru(dad)(MeCN)]²⁺ (11). If the second and further reduction scans are performed after a waiting period at 0.0 V, 11 has diffused into the bulk solution and the new scans do not differ from the first one. Figure 4 shows corresponding cyclic voltammograms.

The easier reduction of the [Ruᴵᴵ]²⁺ complex 11 as compared to the monocation **2** is normal. No further reduction beyond **5** was detectable in the accessible solvent range. There is no indication during either scan direction for a stable five- or six-coordinate Ru(I) species. Lability of the chloro ligands during an irreversible two-electron reduction is also characteristic for (dad)₂RuCl₂.[1] These latter complexes are, however, reversibly oxidized with retention of their starting cis or trans structure. As reported above, the benzene ligand in 7b can be replaced by acetonitrile at ambient temperature. Therefore, it is not surprising

that the benzene ligands in complexes **2** are labilized after oxidation; facile substitution by acetonitrile occurs beyond the first oxidation wave. On the corresponding reverse scan (Ru(III) → Ru(II)) there is of course no cathodic wave for a hypothetical couple 2⁺ → 2, but a new wave at much more negative potentials (see Figure 4) appears for the reduction of [(MeCN)₃Ru(dad)Cl]²⁺ to [(MeCN)₃Ru-(dad)Cl]⁺ (12). These two ions form a reversible redox couple.

The redox behavior of **2** shows that dad ligands, as opposed to π-ligands like benzene or simple σ-donors like Cl⁻ or CH₃CN, stick to the metal in normal and low oxidation states. This was also observed for other dad complexes in competition with ligands such as CO, MeCN, and PR₃.[41] Free dad ligands with aromatic N substituents can be reduced electrochemically in MeCN/TBAP, and even the glyoxal-derived N-alkyl dad ligands like 1a and 1c show reduction waves in the potential range accessible in this solvent.[32] The dad reduction is already facilitated by the presence of K⁺, Na⁺, or Li⁺ ions. The energetic lowering of the dad π^* orbital, which accepts the extra electron as revealed by high-resolution EPR spectroscopy,[22,42] is encountered within all dad metal complexes, where the metal has a dominant Lewis acid character (σ-effect).[22]

Even in dad complexes with M(CO)₄ (M = Cr, Mo, W)[41] fragments, reversible reduction waves occur at more positive potentials than in dad themselves, i.e., the inductive stabilization of the π^* level (σ-effect) by coordination is greater than the destabilization in the antibonding combination of the π^* level and the corresponding metal d orbital (back-bonding). No reduction wave can be detected for the Ru(0) complexes **5**. The antibonding LUMO (b₂ in C_{2v} symmetry, see Figure 5) therefore must have substantial Ru(arene) contributions, and vice versa one of the occupied b₁ orbitals has bonding contributions from the b₁ π^* dad orbital. Back-bonding must be quite important for complexes **5**. In other complexes such as (dad)₂Ni⁰,

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Table VI. Analytical Data for Complexes [(Arene)Ru(dad)X]Y

no.	formula	mol wt	calcd			found		
			C	H	N	C	H	N
2a	$C_{14}H_{22}BClF_4N_2Ru$	441.7	38.07	5.02	6.34	38.16	5.10	6.42
2b	$C_{16}H_{26}BClF_4N_2Ru$	469.7	40.91	5.58	5.96	41.14	5.79	6.03
2c	$C_{16}H_{26}BClF_4N_2Ru$	469.7	40.91	5.58	5.96	40.30	5.63	6.26
2d	$C_{22}H_{22}BClF_4N_2Ru$	537.8	49.14	4.12	5.21	47.52	3.97	5.67
2e	$C_{22}H_{22}BClF_4N_2Ru$	537.8	49.14	4.12	5.21	48.75	4.09	5.40
2f	$C_{24}H_{26}BClF_4N_2Ru$	565.8	50.95	4.63	4.95	50.64	4.77	5.20
2g	$C_{24}H_{26}BClF_4N_2O_2Ru$	597.8	48.22	4.38	4.69	48.72	4.63	4.82
2h	$C_{26}H_{30}BClF_4N_2Ru$	593.9	52.59	5.09	4.72	52.39	5.35	5.81
2i	$C_{24}H_{26}BClF_4N_2Ru$	565.8	50.95	4.63	4.95	51.25	4.74	5.06
2j	$C_{28}H_{33}BClF_4N_3Ru$	634.9	52.97	5.24	6.62	53.13	5.30	6.50[a]
2k	$C_{32}H_{42}BClF_4N_2Ru$	678.0	56.69	6.24	4.13		6.19	3.79
3	$C_{19}H_{32}BClF_4N_2Ru$	511.8	44.59	6.30	5.47	44.05	6.29	5.40
4	$C_{14}H_{22}I_2N_2Ru$	573.2	29.33	3.87	4.89	29.12	3.47	4.30

[a] Anal. Calcd for $[Ru(C_6H_6)(dad)(CH_3CN)](Cl)(BF_4)$.

where likewise reduction could not be achieved electrochemically, the X-ray structure revealed an N–C–C–N skeleton with rather similar NC and CC bond lengths.[23] In the 5 analogue (bpy)Fe(toluene)[20] the structural features are also described in terms of strong ground-state backbonding. The arguments of Albright et al., derived from EH calculations,[19] can be adopted if one accounts for the difference in n^+, n^-, and π^* energies of the dad ligands.

In the isoelectronic complexes (η^5-C_5H_5)Co(dad) finally, the bonding/antibonding contributions between the aromatic ligand, the metal, and the dad are such that the ground state and the excited state of the dominant "charge-transfer" transition probably do no differ in terms of the total molecular dimensions (Cp/dad distance); the metal is simply closer to the one or the other ligand in the relaxed geometry of these states. This situation gives rise to very narrow "charge transfer" absorption,[29] an example of which is given in Figure 3 with comparison to spectra of 5. The half-widths of "CT bands" can be correlated with the actual character of electron transfer or $\pi \rightarrow \pi^*$ transition in model cases.[43]

The intense absorption band in the visible region of the electronic spectra of all dad complexes is assigned to a transition between two orbitals of the same irreducible representation, $2b_1 \rightarrow 3b_1$ in the case of compounds 5. The weak long wavelength shoulder cannot be assigned, since one expects several symmetry-allowed transitions to the LUMO $2b_2$.

Conclusions

The synthesis of (dad)Ru complexes carrying a η^6-arene ligand is straightforward, and the six-coordinate complexes of the type 2 or 7 are highly stable, unless steric hindrance occurs. Reduction of 2 to 5 with concomitant reduction of the coordination number to five leads to remarkably stable compounds. Oxidative addition, e.g., of alkyl iodides, again increases steric strain. This thermodynamically favorable reaction can lead to the loss of η^6-arene ligands, an important feature of these model compounds with respect to catalysis.

Thus, in the catalytic dimerization of butadiene, (dad)Fe^0 systems[8,9] with rather bulky dad N substituents do "work" at 0–20 °C, while with dad 1a or 1d inert intermediates are formed, which have to be heated above 60 °C to perform catalysis. Most catalytic reactions involving alkenes or alkynes constitute consecutive steps of oxidative additions and reductive eliminations.

The half-sandwich compounds 5 differ from complexes (η^6-C_6H_6)Ru(PR$_3$)$_2$, which undergo much faster oxidative additions not only with HX but also with MeI and EtI or Me$_3$SnCl.[16] The basicity of 5 may be lower; at least complexes 5 are less nucleophilic because of steric hindrance. The EHMO description of (arene)ML$_2$ correlates the basicity with the energy of the HOMO, an orbital with antibonding interactions between a filled arene and a filled ML$_2$ fragment orbital.[19]

Lowering of the HOMO energy by bonding contributions of a suitable π^* orbital of the (L$_2$) part of the molecule should reduce the basicity according to the arguments of Albright et al.[19] It must be pointed out, however, that substantial interaction with an (L$_2$) π^* orbital will not only lower the HOMO energy but also increase the delocalization. A substantial delocalization was inferred from the structural data of (η^6-toluene)Fe(bpy), the only example of an X-ray structure of an (arene)ML$_2$ complex with a chelating N ligand.[20] Protonation, on the other hand, requires the localization of the electron pair in a M–H bond. The basicity of (arene)ML$_2$ complexes with the same HOMO energies, e.g., the same first ionization potential in the gas phase, may differ considerably. On the basis of photoelectron spectroscopic data, differences in the HOMO energies have also been pointed out by Green et al.[44] for CpM(diene) complexes, depending on the metal (M = Co, Rh, Ir). We are presently investigating the photoelectron spectra of (arene)M(dad) complexes.

Experimental Section

The synthesis of 1,4-diaza-1,3-dienes was performed according to literature procedures.[28,32,45–47] "RuCl$_3$·3H$_2$O" (35% Ru) was obtained from Degussa, Hanau, FRG. The benzene complex [Ru(C$_6$H$_6$)Cl$_2$]$_2$ was prepared according to Bennett et al.[14a] AgBF$_4$ was purchased from Fluka, Karlsruhe, FRG. All operations were performed under an inert-gas atmosphere; solvents were thoroughly dried and stored under inert gas. The acetonitrile for electrochemical measurements was purified as described in ref 48, stored over CaH$_2$ in a brown glass cyclic distillation apparatus, and always freshly distilled before use.

Benzene Ruthenium(II) Complexes 2. General Procedure. A solution of 2 mmol of AgBF$_4$ in 20 mL of MeCN was slowly added dropwise to a suspension of 1 mmol of [Ru(C$_6$H$_6$)Cl$_2$]$_2$ in 50 mL of MeCN. The solution gradually turned yellow, and AgCl was precipitated. Stirring was continued for 1 h after the addition of the silver salt solution, and then the AgCl was separated by filtration. An excess of 1.5–2 mmol of dad 1a–k was added to the yellow-orange solution, and the mixture was boiled for 3 h. The now dark red solution was cooled, filtered once more, and then concentrated by evaporation under reduced pressure to a total of 10 mL. The products 2 were precipitated by adding

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(48) Walter, M.; Ramaley, L. *Anal. Chem.* **1973**, 45, 165.

Table VII. Analytical Characterization of Complexes 5–8

no.	formula	mol wt	calcd H	calcd N	found H	found N	subl temp, C	mass spectrum,[a] m/e		
5a	$C_{14}H_{22}N_2Ru$	319.4	6.94	8.77	6.35	8.47	80–100	319 (17)	320 (29)	322 (15)
5b	$C_{16}H_{26}N_2Ru$	347.5	7.54	8.06	7.12	7.34	80[b]	347 (15)	348 (30)	350 (16)
5c	$C_{16}H_{26}N_2Ru$	347.5					80–100	347 (16)	348 (29)	350 (16)
5e	$C_{22}H_{22}N_2Ru$	415.5	5.34	6.74	4.96	6.59	180	415 (18)	416 (26)	418 (14)
5f	$C_{24}H_{26}N_2Ru$	443.6	5.91	6.32	5.11	5.75	160–200			
6	$C_{19}H_{32}N_2Ru$	389.5					100			

no.	formula	mol wt	calcd C	calcd H	calcd N	found C	found H	found N
7a	$C_{15}H_{25}IN_2Ru$	461.3	39.05	5.46	6.07	38.47	5.41	5.97
7b	$C_{17}H_{29}IN_2Ru$	489.4	41.72	5.97	5.72	41.79	6.29	5.62
7e	$C_{23}H_{25}IN_2Ru$	557.4	49.56	4.52	5.03	47.90	4.42	4.81
7f	$C_{25}H_{29}IN_2Ru$	585.5	51.29	4.99	4.78	52.65	4.68	4.91
8a	$C_{19}H_{27}IN_2Ru$	475.4	40.43	5.73	5.89	40.56	5.80	5.85

[a] Parent ions; given are the three most intense isotopic peaks with relative intensity ($\sum M^+ = 100$); sample temperature 30 °C, 70 eV. [b] Condensation from molten 5b.

diethyl ether, separated, washed with Et_2O to remove traces of 1, and dried under vacuum; yields 40–75%. Recrystallization is possible from $MeCN/Et_2O$, Me_2CO/Et_2O, or CH_2Cl_2/petroleum ether. Analyses are collected in Table VI.

(η^6-**Benzene)(glyoxal bis(isopropylimine))iodo-ruthenium(II) iodide (4)** was prepared from 5a (30 mg, 0.09 mmol) in 25 mL of diethyl ether by the slow addition, with stirring, of 20 mg (0.16 mmol) of iodine. A yellow-brown precipitate formed immediately, which was separated, washed with ether, and dried under vacuum. 4 resembles compounds 2 in most properties. See Table VI for analysis.

(η^6-**1,2-Diethyl-4-methylbenzene)(glyoxal bis(isopropyl-imine))chlororuthenium(II) Tetrafluoroborate (3).** In analogy to the preparation of $[(C_6H_6)RuCl_2]_2$, 450 mg of $RuCl_3\cdot3H_2O$ (1.6 mmol of Ru) was refluxed in 15 mL of ethanol with 1.5 mL of 1,2-diethyl-4-methyl-1,4-cyclohexadiene. The diene was obtained catalytically from isoprene and 3-hexyne.[7] The hot, brown-red, Ru-containing solution was filtered, the solvent removed under vacuum, and the solid residue thoroughly washed with diethyl ether and finally with petroleum ether. The yield of the $[(\eta^6\text{-arene})RuCl_2]_2$ was 210 mg (42%).

According to the general procedure for complexes 2 210 mg (0.33 mmol) of $[(1,2\text{-}(Et)_2\text{-}4\text{-}MeC_6H_3)RuCl_2]_2$ was stirred with $AgBF_4$ in acetonitrile. The resulting yellow solution, after filtration, was concentrated to 2 mL, then 30 mL of THF and 170 mg (1.2 mmol) of dad 1a were added, and the resultant solution was heated once to boiling, concentrated under vacuum, and treated with diethyl ether to precipitate 3. Recrystallization from dichloro-methane/diethyl ether gave 250 mg (0.49 mmol, 74%) of 3. See Table VI for analysis.

(η^6-**Benzene)(diazadiene)ruthenium(0) Complexes (5). General Procedure a.** To a solution of 1 mmol of complex 2 in 20 mL of THF was added a THF solution containing 2 mmol of sodium naphthalene ($\sim$0.2 N solution in THF).

After the solution was stirred for 30 min, the solvent was removed and the major part of free naphthalene eliminated by sublimation at 30–40 °C under high vacuum. The residue was extracted with 50 mL of n-hexane (N-alkyl dad) or toluene (N-aryl dad) and filtered from insoluble material; the solution was once more evaporated to dryness. Residual naphthalene was sublimed at ambient temperature, and then the product was purified by sublimation between 80 (5a–c) and 200 °C (5e,f). Recrystallization was performed from n-hexane and toluene/n-hexane, respectively. The crystalline, red complexes were obtained in yields from 60 to 75%.

b. Instead of starting from complexes 2, complexes 5a and 5c were obtained directly from $[Ru(C_6H_6)Cl_2]_2$ (0.5 mmol, 250 mg) and dad 1a/c (1.0 mmol) in 40 mL of THF and 2 mmol sodium naphthalene (as 0.2 N solution in THF). Further treatment was parallel to procedure a; dad from uncomplete reactions sublimed also under vacuum. The final yields in this reaction were much lower (10–25%).

Complex 5b has its melting point only slightly above room temperature; purification from naphthalene was difficult. Analytical results of the very air-sensitive complexes were unsatis-

factory for carbon; H and N values were rather better. The characterization of the volatile complexes 5 was readily possible by mass spectrometry (Table VII). The mass spectrum showed the parent ion (^{102}Ru) as the basis peak; $[Ru(dad)]^+$ and $[Ru(C_6H_6)]^+$ appeared with 40–60% intensity.

(η^6-**Benzene)(diazadiene)(σ-alkyl)ruthenium(II) Iodide Complexes (7 and 8). General Procedure.** About 0.3 mmol of complexes 5 or 6 in 50 mL of n-hexane was stirred with an excess (2 mL) of alkyl iodide. The reaction rate of the formation of an unsoluble precipitate of 7 and 8 depended largely on the size of the dad, the arene, and the incoming alkyl group. MeI reacted within 2 (7a) to 5 (7f) h and EtI within 7 (8a) to 40 days (8x) at room temperature. The separated precipitates were re-crystallized from dichloromethane/petroleum ether. The yields were 75–95%.

The chiral [(η^6-1,2-diethyl-4-methylbenzene)(glyoxal bis(iso-propylimine))(σ-ethyl)ruthenium] iodide (8x) was characterized via its very informative 360-MHz ^1H NMR spectrum (see Table II).

(η^6-**Benzene)(glyoxal bis(isopropylimine))(η^2-ethylene)-ruthenium(II) Tetrafluoroborate (9).** The σ-ethyl complex 8a (240 mg, 0.5 mmol) was dissolved in 15 mL of dichloromethane, and a slight excess of triphenylmethyl tetrafluoroborate (185 mg, 0.6 mmol) was added. After the mixture was stirred for 3 h, an equivalent of $NaBF_4$ was added and stirring was continued for 1 day. The yellow precipitate was analytically pure 9 and gave good analytical results.

The formation of [tris(acetonitrile)(biacetyl bis(isopropyl-imine))(σ-methyl)ruthenium(II)] iodide (10) from 7b in aceto-nitrile-d_3 at room temperature was followed by ^1H NMR spec-troscopy and was complete after 4 days. No efforts have been made to isolate complex 10.

Reaction of 2a with Methylmagnesium Iodide. To a so-lution of 100 mg (0.23 mmol) of 2a in 20 mL of diethyl ether was added 0.27 mmol of CH_3MgI in ether. The solution turned yellow immediately and showed a turbidity. After several hours of stirring, the solvent was evaporated in vacuo and the residue was extracted with two portions of dichloromethane (5-mL each). The filtered extracts were again taken to dryness, redissolved in CD_2Cl_2, and analyzed by ^1H NMR spectroscopy: 45% of the chloro complex 2a, with probably iodide as a counterion, 45% of the iodo iodide 4, and only 10% of the methylated cation 7 were formed.

Physical Measurements. Electronic spectra were recorded with a Perkin-Elmer spectrophotometer 554. ^1H NMR experi-ments were run on a Bruker WP 80 SYFT, a Bruker WH 270, a Bruker WH 400 (with computer aspect 2000), or a Bruker AL 360 spectrometer (with computer aspect 3000), depending on the resolution or software requirements. Cyclic voltammetry was performed by using a PAR electrochemistry system Model 170. Details on the electrodes and referencing were reported earlier.[1]

The oxidation and reduction of complexes 2 are chemically irreversible. Scan rates from 20 to 200 mV/S have been applied; all scans have been repeated to include or exclude certain waves; waiting periods were introduced to allow electrochemically formed products to diffuse into the bulk solution. Mass spectra were

recorded with a Varian CH7 spectrometer (push rod, sample temperature 30 °C, 70-eV electron energy).

# Deviation from the Ideal Octahedral Field vs. Alkyl Distortion in d⁰ Metal–Alkyl Complexes: A MO Study

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The main geometrical features of d⁰ hexacoordinated alkyl complexes (R = CH₃, C₂H₅) are analyzed by means of extended Hückel calculations. Structural distortions from the ideal octahedral field around the metal and distortions at the organic ligand (agostic group) are discussed. The following are shown. (i) The octahedral ligand field around the d⁰ hexacoordinated complex is not a minimum on the potential energy surface. Distortions entailing mixing with low-lying empty d orbitals do occur (second-order Jahn–Teller effect); however, π-donor groups at the metal (chlorine atoms, for instance) help the system to remain close to the octahedron. (ii) Distortions at the organic ligand and around the metal center are antagonizing each other when they occur in the same plane, because they make use of the same vacant metal orbital to stabilize some occupied MO's (in particular the HOMO of the complex). (iii) While the metal C–H interaction is very weak in the methyl complex, it is less so in the ethyl complex, in good agreement with experimental evidence.

The geometrical features of some electron-deficient organometallic complexes suggest an interaction between the metal center and a nearby C–H bond carried by an organic ligand. The group that brings this C–H bond has been called "agostic" by Brookhart and Green.[1] In some cases this interaction is made at the expense of a strong structural distortion of the organic ligand. In particular, octahedral complexes 1 and 2 exhibit unusually small M–
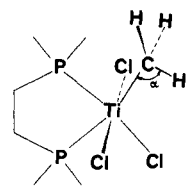
1

(α = 93.7°)
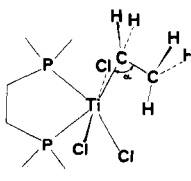
2

(α = 85.9°)

C–H angles (93.7° for 1 and 85.9° for 2, respectively), suggesting a strong driving force for the distortion of the

methyl (1) or the ethyl (2) groups.[2] The main chemical interest of these complexes is that they may be regarded as models for the transition states of α (1) and β (2) oxidative addition. Indeed, both 1 and 2 are characterized by a rather short Ti···H distance and by a weakening of the C–H bond interacting with the metal. Related distortions for alkylidene groups have been reported by Schrock and co-workers.[3] Several theoretical studies have been devoted to the understanding of this fascinating class of compounds.[4]

However, the alkyl distortion is not the only structural characteristic of these complexes. One can also note a strong deviation from the ideal octahedral field around the metal center, in both 1 and 2. While two metal–chlorine bonds remain almost exactly perpendicular to the alkyl distortion plane, ligand angles in that plane are far from the ideal 90° value. In particular, the C–Ti–Cl angle is larger (114° in 1 and 128.4° in 2, respectively), while the opposite phosphine angle is only 75°. It may be asked

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