same as found in R_2PS^- complexes, in which the ligand forms a $MP(R_2)SM$ bridge between two metal atoms.[5,9] The coordination around the molybdenum atom can be regarded as a pentagonal bipyramid with both CO groups on the axial positions and the three P atoms and the two S atoms in the equatorial plane. The deviations from the least-squares plane through Mo, P(1), P(2), P(3), S(1), and S(2) are as follows: (in Å): 0.003 for Mo, 0.07 for P(1), 0.007 for P(2), -0.06 for P(3), -0.06 for S(1), and 0.04 for S(2).

In this compound the oxidation state of Mo is II, when both $SPPh_2^-$ ligands are considered to be uninegative 4-electron donors. The complex obeys the 18-electron rule. It is interesting to note the structural similarity between IX and the 18-electron compounds like $IrCl(PPh_3)_2(\eta^2\text{-}C_2H_4)_2$ and $IrCl(PPh_3)_2(\eta^2\text{-}O_2)(\eta^2\text{-}C_2H_4)$.[26,27] To stress this point, an alternative description of this complex as having a Mo(-II) center (d^8 as with Ir(I)) with two unipositive 2-electron-donor $SPPh_2$ ligands is possible. Although this alternative description is illustrative, we prefer Mo(II) rather than a Mo(-II), because we think that II is a more realistic indication of the electron density distribution.

Acknowledgment. The authors wish to thank Prof. Dr. Ir. J. J. Steggerda for stimulating discussion, P. J. J. Koonen for performing the C, N, H analyses, and P. P. J. Schlebos and H. H. K. Brinkhof for recording the ^1H NMR and ^{31}P NMR spectra.

Registry No. Ia, 90967-97-8; Ib, 90967-98-9; IIA, 90967-99-0; IIB, 90968-00-6; III, 90968-01-7; IVa, 90968-02-8; IVb, 91002-34-5; V, 76380-95-5; VI, 76374-51-1; VII, 90990-39-9; VIII, 90990-40-2; IX, 76375-06-9; X, 76374-49-7; XI, 90968-03-9; $Mo(CO)_3(\eta^5\text{-}C_5H_5)Cl$, 12128-23-3; $W(CO)_3(\eta^5\text{-}C_5H_5)Cl$, 12128-24-4; $Ph_2P(S)C(S)N(H)Ph$, 7067-81-4; $Ph_2P(S)C(S)N(H)Me$, 14825-33-3; $SPPh_2H$, 6591-07-7; $Mo(CO)_3(PPh_3)_2Cl_2$, 17250-39-4; $W(CO)_3(PPh_3)_2Cl_2$, 18130-04-6; $Mo(CO)_4Cl_2$, 15712-13-7.

Supplementary Material Available: Listings for $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ of structure factors, thermal parameters of the non-hydrogen atoms, and the fractional coordinates of the hydrogen atoms attached to the phenyl carbon atoms, stereo plots of $Mo(CO)_2(\eta^5\text{-}C_5H_5)[Ph_2P(S)C(S)NPh]$ and $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2\cdot CH_2Cl_2$, and a plot of the molecular structure of $Mo(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2$ (26 pages). Ordering information is given on any current masthead page.

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Ruthenium Complexes with Diazabutadienes. 3.[1] Trans and Cis Isomers of Dichlorobis(diazabutadiene)ruthenium, $(RN{=}CR'{-}CR'{=}NR)_2RuCl_2$

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Received March 1, 1983

The preparation of a series of (diazabutadiene)ruthenium complexes, $(dad)_2RuCl_2$ (dad = RN=CR'-CR'=NR (R' = H, CH_3; R = C_6H_5, substituted phenyl group)), is described. In a thermal reaction starting from tetrakis(benzonitrile)dichlororuthenium, blue or green *trans*-$(dad)_2RuCl_2$ are formed first, which isomerize above 130 °C to the violet cis complexes. Electron spectroscopic, ^1H NMR, and electrochemical data are discussed with respect to symmetry and conformation of the complexes formed. Cis complexes with ligands derived from biacetyl (R' = CH_3) show unusual chemical shifts for aromatic ortho protons, indicating a rigid *N*-phenyl conformation. Two rotational barriers for symmetry-independent aromatic substituents are detected. While the Ru(II)-Ru(III) redox process is fully reversible for both stereochemistries, the reduction is irreversible. The trans → cis isomerization can be achieved catalytically by electron transfer. The otherwise very inert chloro ligands can easily be substituted at potentials below the irreversible reduction step to give, for example, in the presence of free dad and after reoxidation complexes $[Ru(dad)_3]^{2+}$.

Introduction

The coordination chemistry of 2,2'-bipyridine (bpy) has been, by far, more extensively investigated than the coordination chemistry of the related diazabutadiene (dad) ligand system; this is especially true for ruthenium, since research interests focused on the potential applications of tris(bipyridine)ruthenium ions in the photochemical water-splitting reaction.[2] It has only recently become clear that the diazadienes show a much wider range of coordination modes and reaction types[3,4] than bpy. Other advantages that can be ascribed to the diazadiene system are (i) simple synthesis from inexpensive starting materials,[5a,b] (ii) broad variability of substituents including chiral groups,[6] (iii) simple theoretical description of the small -N=C-C=N- system,[7] and (iv) enhanced solubilities as compared to many analogous bpy complexes.

The stereochemistry of the important starting materials bis(bipyridine)$(L)_2$ruthenium(II) was reinvestigated recently, and the trans isomer $(bpy)_2RuCl_2$ is still a poorly characterized material because of its extreme insolubility.[8] Despite the fact that there is no literature evidence for octahedral complexes with two trans dad ligands, we knew, from our stereochemical studies with other coordination geometries, that these should be accessible with relatively small N substituents.[5b] We report here on the synthesis of bis(diazabutadiene)dichlororuthenium complexes with N aromatic substituents, on their trans-cis

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isomerization, and on their conformational and spectroscopic behavior.

Experimental Section

Ruthenium trichloride hydrate, $RuCl_3 \cdot xH_2O$ (35.7% Ru) from Degussa (Hanau, Germany) was used without further purification. Solvents were purified and dried according to standard procedures. All reactions were carried out under dry N_2 to prevent eventual oxidation or hydrolysis. All diazadiene ligands were prepared as described previously from the appropriate aniline, biacetyl, or aqueous glyoxal.[5a,b]

$Ru(C_6H_5CN)_4Cl_2$. The synthesis reported by Newton and Searles[9] was modified: 2 g of $RuCl_3 \cdot 3H_2O$ (containing 7 mmol of Ru), dissolved in 50 mL of methanol, was refluxed for 3 h after the addition of 10 mL of benzonitrile. The cooled solution was then agitated, together with 20 mg of PtO_2, under a hydrogen atmosphere. After the uptake of the calculated amount of H_2, the solvents were evaporated in vacuo and the residue was washed with ether. The raw material was then dissolved in 80 mL of warm dichloromethane, and the resultant mixture was filtered. Careful addition of ether precipitates the benzonitrile complex in good yield (3.7 g, 90% average over several runs).

The yields and the isomeric composition, in cases where the cis isomers are sterically accessible, of the complexes described below depend strongly on the reaction time. Typical results are given.

***trans*-Ru[C_6H_5N=C(CH_3)—C(CH_3)=NC_6H_5]$_2Cl_2$ (2a) and *cis*-Ru(N⌒N)$_2Cl_2$ (3a).** $Ru(C_6H_5CN)_4Cl_2$ (0.5 g, 0.9 mmol) was heated to the boiling point of the solvent diglyme (50 mL), in the presence of a slight excess of biacetyl bis(phenylimine) (**1a**) (0.5 g, 1.9 mmol), within a period of 30 min. After boiling for further 5 min, the solution was cooled. Fine crystals of **2a**, with a brasslike luster, separated from the deep blue solution within 3 days at −20 °C. The collected crystals were washed with acetone to remove traces of violet **3a** and dried in vacuo (yield 33%). Anal. Calcd for $RuC_{32}H_{32}N_4Cl_2$: C, 59.6; H, 5.0; N, 8. Found: C, 58.4; H, 4.7; N, 7.9. The diglyme mother liquid was again heated under reflux for 3 h, and the color changed from blue to violet. Diglyme was then removed under vacuum, the excess ligand was extracted from the residue with petroleum ether (2 × 20 mL), and the product was then dissolved in dichloromethane. Addition of petroleum ether (30–50 °C) gave a precipitate of small black-violet crystals of **3a** in 38% yield. Found: C, 59.5; H, 5.1; N, 8.5.

***trans*-Ru[4-CH_3-C_6H_4N=C(CH_3)—C(CH_3)=NC_6H_4-4-CH_3]$_2Cl_2$ (2b) and *cis*-Ru(N⌒N)$_2Cl_2$ (3b).** Similar to the procedure described for **2a**/**3a**, $Ru(C_6H_5CN)_4Cl_2$ was heated with a slight excess of biacetyl bis(4-methylphenylimine) (**1b**), this time for 1 h in boiling diglyme. The trans complex **2b** crystallized overnight at ambient temperature (yield 28%) from the blue-violet solution. Further heating of the filtrate gave 32% of **3b**. Anal. Calcd for $RuC_{36}H_{40}N_4Cl_2$: C, 61.7; H, 5.8; N, 7.8. Found for **2b**: C, 61.2; H, 5.8; N, 7.8. Found for **3b**: C, 61.1; H, 5.8; N, 7.8.

***trans*-Ru[3,5-$(CH_3)_2$-C_6H_3N=C(CH_3)—C(CH_3)=NC_6H_3-3,5-$(CH_3)_2$]$_2Cl_2$ (2c) and *cis*-Ru(N⌒N)$_2Cl_2$ (3c)** were prepared as **2b**/**3b** with yields of 35% for the blue **2c** and 45% for violet **3c**. Anal. Calcd for $RuC_{40}H_{48}N_4Cl_2$: C, 63.5; H, 6.4; N, 7.4. Found for **2c**: C, 62.9; H, 6.4; N, 7.3. Found for **3c**: C, 62.5; H, 6.5; N, 7.3.

***trans*-Ru[2,6-$(CH_3)_2$-C_6H_3N=C(CH_3)—C(CH_3)=NC_6H_3-2,6-$(CH_3)_2$]$_2Cl_2$ (2d).** Even after prolonged heating of the benzonitrile complex with ligand **1d**, the blue color of **2d** persists (yield 63%). Anal. Calcd for $RuC_{40}H_{48}N_4Cl_2$: C, 63.5; H, 6.4; N, 7.4. Found: C, 63.8; H, 6.6; N, 7.2.

***trans*-Ru[2,6-$(CH_3)_2$-C_6H_3N=CH—CH=NC_6H_3-2,6-$(CH_3)_2$]$_2Cl_2$ (2e).** This glyoxal-derived complex again showed no tendency to form the corresponding cis complex after several hours of boiling in diglyme; yield of **2e** 73%.

***trans*-Ru[4-CH_3-C_6H_4N=CH—CH=NC_6H_4-4-CH_3]$_2Cl_2$ (2f) and *cis*-Ru(N⌒N)$_2Cl_2$ (3f).** Refluxing $Ru(C_6H_5CN)_4Cl_2$ with glyoxal bis(4-methylphenylimine) (**1f**) in a 1:2.2 molar ratio for 5 h in THF gave **2f** (green crystals) in 76% yield after washing off traces of **1f** with petroleum ether (30–50 °C) and drying. Heating **2f** for 3 h in refluxing diglyme gave the corresponding cis complex **3f** in almost quantitative yield.

***trans*-Ru[4-CH_3O-C_6H_4N=CH—CH=NC_6H_4-4-OCH_3]$_2Cl_2$ (2g) and *cis*-Ru(N⌒N)$_2Cl_2$ (3g).** As in the case of **2f**, the trans complex was prepared first by thermal reaction with ligand **1g** in boiling THF. The isomerization was then performed in boiling diglyme to yield quantitatively the cis complex **3g**. Good analytical results were obtained for the glyoxal-derived complexes.

[(4-CH_3-C_6H_4N=CH—CH=NC_6H_4-4-CH_3)$_3$Ru](PF$_6$)$_2$ (4). Complex **2f** (220 mg, 0.34 mmol) was stirred with 90 mg (0.38 mmol) of **1f** and 18 mg of sodium (0.76 mmol) for 2 days at 50 °C in 30 mL of THF. Iodine (100 mg, 0.78 mmol) was added to the brown solution and the red-brown precipitate of $Ru(dad)_3I_2$ collected on a filter. For purification, the iodide was dissolved in hot ethanol and a slight excess of NH_4PF_6 added. The hexafluorophosphate **4** separated in the form of very dark crystals after the solution was cooled (350 mg, 94%). ^1H NMR (CD_3CN): 8.47 (6 H, s), 7.19 (12 H, d), 6.10 (12 H, d, J = 8 Hz), 2.40 ppm (18 H, s). UV (CH_3CN): λ_{max} 544, 510 nm.

Physical Measurements. Electronic spectra were recorded with a Perkin-Elmer spectrometer 554. NMR spectra were recorded on a Bruker WP 80 SY FT spectrometer (80 MHz) using different techniques for assignments of correlated protons including DID methods.[10] Cyclic voltammetry was performed by using a PAR electrochemistry system Model 170; measurements were done in dichloromethane or acetonitrile with use of a Pt electrode and an Ag(s)/$AgNO_3$ (0.1 M) CH_3CN reference, which is +0.30 V against SCE for CH_3CN solutions and +0.19 V for CH_2Cl_2 solutions (ferrocene pilot ion method). Acetonitrile was purified according to literature procedures[11] and freshly distilled under nitrogen in a brown-glass system. Several of the trans complexes have such a poor solubility in CH_3CN that, in order to obtain good voltammograms, they were first oxidized in a very slow coulometric experiment to the soluble $[(dad)_2RuCl_2]^+$ cation and then the cyclic voltammetry was performed.

The reduction of Ru(II) complexes **2** and **3** is completely irreversible in CH_2Cl_2. In CH_3CN a small anodic wave is observed at a scan rate of 200 mV/s. After the addition of ligand **1f** to solutions of **2f** or **3f** and the scan is extended to about −1.8 V, the anodic waves of Ru(0) → Ru(I) at −1.07 V, of Ru(I) → Ru(II) at −0.68 V, and of Ru(II) → Ru(III) at +1.30 V are detected, which are identical with the $E_{p,a}$ positions of the chemically prepared complex **4**.

Results

A series of ruthenium(II) complexes of the type *trans*-dichlorobis(diazabutadiene)ruthenium (**2a–g**) and *cis*-dichlorobis(diazabutadiene)ruthenium (**3a–c,f,g**) are obtained by thermal reaction of *trans*-$Ru(C_6H_5CN)_4Cl_2$ with the corresponding 1,4-diaza-1,3-diene (**1a–g**, dad). Some dads (**1f,g**) react in boiling tetrahydrofuran to give, in a kinetically controlled reaction, the trans complexes (**2f,g**) exclusively. In other cases the reactions have to be performed in hot or boiling diglyme (130–160 °C) in order to drive the reaction beyond the red intermediate (probably $Ru(dad)(C_6H_5CN)_2Cl_2$). Under these more severe conditions, a mixture of *trans* and cis complexes is obtained from **1a–c**; **2f,g** isomerize to the cis complexes **3f,g**. Compounds **2d,e** do not isomerize to the corresponding cis complexes, even after very long heating at 162 °C. The blue (**2a–e**) or green (**2f,g**) trans compounds are less soluble than their cis analogues, which makes separation quite simple (Scheme I).

Although the N substituents in **1a–g** seem to be quite bulky, it is evident that they can (or must) be turned out of the dad plane and thus make interligand repulsion in trans **2a–g** relatively small. Under rather special conformational conditions (see below), the same is true for the cis stereochemistry, which is impossible with ligands carrying ortho substituents on the aromatic rings (**1d,e**).

The stereochemistry of the complexes is unequivocally established by NMR spectroscopy (see below). In all cases the trans complexes are formed first. The thermal isomerization irreversibly leads to cis complexes (**3a–c,f,g**). Thermal reaction or irradiation of such cis complexes did not show measurable

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Table I. Electron Spectroscopic Data of *cis*- and *trans*-$Ru(dad)_2Cl_2$ in CH_2Cl_2

compd	λ, nm (ε, M^{-1} cm^{-1})				
2a	755 (1700)	661 (11 100)	520 (1100)	340 (1800)	265 (10 700)
2b	765 (1400)	662 (11 000)	528 (1600)	375 (2200)	
2c	765 (1500)	658 (12 000)	525 (1200)	360 (1800)	265 (11 800)
2d	783[d] (1700)	615 (12 000)	...	370 (1200)	
2e	765 (1800)	645 (8400)	...	385[a] (1100)	250 (4600)
2f	810 (2000)	702 (9400)	546 (700)	430[b] (11 300)	265[c] (13 700)
2g	820 (0.07)	705 (0.5)	630 (0.05)	470 (0.8)	340 (0.7)[e]
3a	...	554 (12 200)	464 (3000)	310 (7000)	280 (8800)
3b	...	556 (12 000)	462 (3100)	320 (7500)	280 (9400)
3c	...	556 (12 300)	464 (2900)	310 (7100)	280 (8900)
3f	...	572 (8900)	478 (2700)	370 (15 000)	305 (7400)
3g	...	585 (0.33)	...	407 (0.85)[e]	

[a] Shoulder at 320 (1500). [b] Shoulder at 308 (9500). [c] Further shoulders at 404 (9300) and 385 (7000). [d] Further shoulder at 710 (1850). [e] Relative intensities.

quantities of trans compounds. Even at temperatures as high as 135 °C, no enantiomeric exchange could be detected by spin–saturation transfer experiments, which of course does not exclude racemization type processes on a preparative time scale at this temperature.

The isomerization of trans complexes of type **2** to the thermodynamically more stable cis complexes of type **3** can easily be followed by electron spectroscopy and shown to be a first-order reaction. The decrease of the main CT component at 680 nm of **2b** is accompanied by the increase of the 560-nm band of **3b** in boiling chlorobenzene (132 °C), with $\tau_{1/2} \sim 50$ min (Figure 1).

All trans complexes show a main CT band with λ_{max} in CH_2Cl_2 between 615 and 702 nm ($\epsilon \sim 10^4$ M^{-1}·cm^{-1}) and less intense shoulders on each side; cis complexes show their main transition shifted to shorter wavelengths (554–572 nm, $\epsilon \sim (9–12) \times 10^3$ M^{-1}·cm^{-1}) with one accompanying band on the short-wavelength side (Table I). The bands are slightly solvatochromic.

The stereochemistry of complexes **2** is reflected in their simple ^1H NMR spectra, which show equivalence for all substituents on nitrogen or carbon in agreement with D_{2d} symmetry. Stereo models do require the noncoplanarity of the aromatic N substituents to accommodate two dads in this geometry. Substituents in the ortho positions of the aromatic rings still show some influence in the visible spectra of the complexes but no special influence on the NMR spectra (see Table II).

The ^1H NMR spectra of the corresponding cis complexes **3** are quite different. This is due not only to the lower symmetry of these compounds (C_2) but also to the unusual

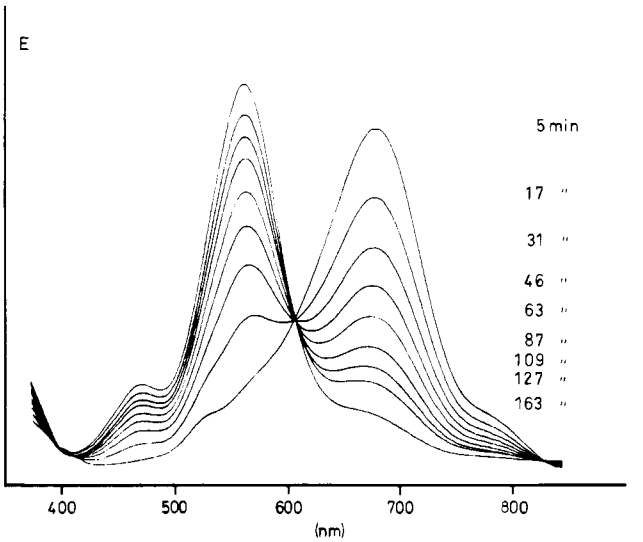

Figure 1. Trans → cis isomerization **2b** → **3b** in boiling chlorobenzene (132 °C) as followed by electron spectroscopy.

Scheme I

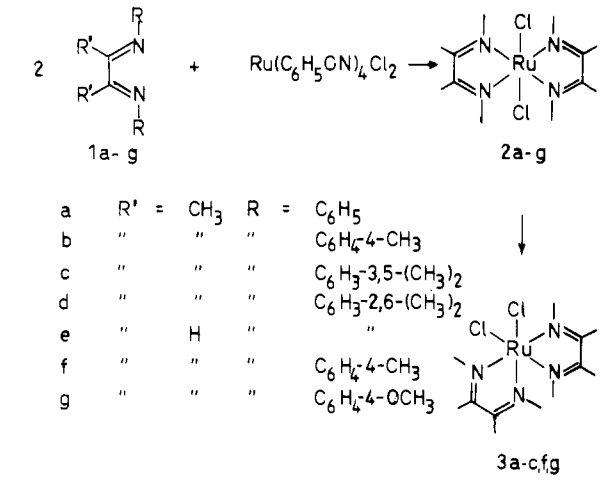

Table II. ^1H Chemical Shift Data (δ, Relative to Internal Me_4Si) of the N Substituent Protons of $(dad)_2RuCl_2$ (Assignment of Primed and Unprimed Set according to Figure 5)

compd	ring substituents	positions 2	6	3	5	4	2'	6'	3'	5'	4'	R/R'[a]		temp, K	solvent
2a	...			6.6–7.0			...	...	...	...	...	2.05		305	$CDCl_3$
3a	...	7.73	4.90	7.3	7.0	7.15	6.75	6.45	7.65–7.43			2.30	2.16	240	DMF
		6.62		7.2			6.77		7.5			2.22		400	DMF
2b	4	6.62		6.69		2.32	...	...	...	...	...	2.06		305	$CDCl_3$
3b	4,4'	7.62	4.93	6.82	7.05	2.11	6.64	6.27	7.27	7.36	2.23	2.47	2.23	270	DMF
	4,4'	6.53		7.00		2.16	6.62		7.34		2.26	2.54	2.36	410	DMF
2c	3,5	6.40		2.18		6.64	...	...	...	...	...	2.18		305	CD_2Cl_2
3c	3,5, 3',5'	7.35	4.78	2.33	2.38	6.76	6.46	5.92	2.19		7.16	2.11	2.29	305	DMF
	3,5, 3',5'	5.9–6.5		2.37		6.77	5.9–6.5		2.22		7.13	2.11	2.27	393	DMF
2d	2,6	1.94		6.65		6.98	...	...	...	...	...	1.99		305	CD_2Cl_2
2e	2,6	2.02		6.70		6.99	...	...	...	...	...	8.39		305	$CDCl_3$
2f	4	6.67		7.08		2.25	...	...	...	...	...	8.61		305	$CDCl_3$
3f	4,4'	6.63		7.0[b]		2.34	7.0[b]		7.11[b]		2.39	8.34	8.49	305	$CDCl_3$

[a] R/R' = H or CH_3 from glyoxal or biacetyl part. [b] Assignment to primed or unprimed set is arbitrary.

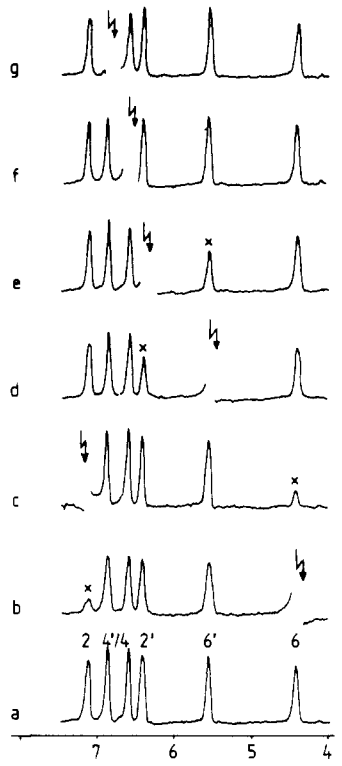

Figure 2. ^{1}H NMR spectrum (a) of and spin-saturation transfer experiments (b–g) on **3c** ($CDCl_3$, 80 MHz, 305 K). Arrows show position of irradiation, a cross-marks responding signal.

chemical shift values of aromatic protons and their temperature dependence. In Figure 2 the ^{1}H NMR spectrum of **3c** is shown. Because of the two meta methyl substituents, no large coupling constants of aromatic protons could be expected. The spectrum at room temperature shows six well-separated signals for the 12 aromatic ortho and para protons, which are spread out over a 3 ppm range. This must mean that the two ortho protons of each ring are nonidentical because of hindered rotation.

Even at 393 K, no limiting spectrum of a complex with freely rotating rings could be obtained. Therefore, a series of spin-saturation transfer experiments were performed, the results of which are also shown in Figure 2b–g. Thus, the highest field signal at 4.4 ppm is correlated to the signal at 7.2 ppm (Figure 2b). The same result is obtained from the reverse irradiation experiment, so that these two signals constitute a pair of ortho protons (6,2) on one ring. A second pair of ortho protons is revealed by the spectra shown in Figure 2d,e (ortho protons 6′,2′), although the response of these ortho protons in the experiment is much less pronounced, indicating a higher rotational barrier. As expected, the signals attributed to para protons 4,4′ show no pairwise correlation. Rough calculations from the temperature-dependent spectra indicate a barrier of 68 ± 5 kJ/mol for the unprimed set and 81 ± 5 kJ/mol for the primed set of signals.

A more detailed assignment is possible for **3b**, for which decoupling experiments at 270 K allow the assignment of ortho and meta protons of one set. Spin-saturation transfer and temperature-dependent spectra finally allow for the assignment of a complete primed and unprimed set. Figure 3a–f reveals more clearly than do the spin-saturation transfer experiments depicted in Figure 2 the different rotational barriers for the two nonequivalent aromatic substituents in C_2 symmetry. Starting from the limiting spectrum shown in Figure 3a, which is consistent with a rigid conformation at 270 K, the signals for the magnetically very different protons 6,2 as well as the signals for the rather similar meta protons 3,5 begin to broaden

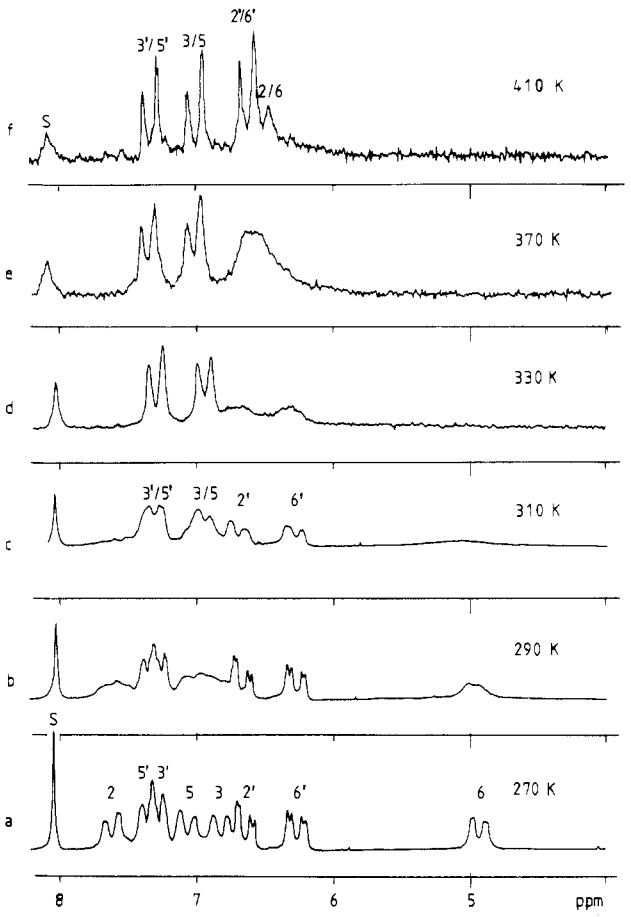

Figure 3. Temperature-dependent ^{1}H NMR spectrum of **3b** in dimethylformamide-d_7 at 80 MHz (aromatic protons only).

around 290 K, while all signals of the primed set are still sharp.

At 330 K, 2′,6′ are still different, while both the 3,5 and the 3′,5′ pairs already show the new limiting spectrum because of their smaller chemical shift differences. At about 410 K the normal NMR spectrum of two AA′BB′ spin systems is observed. The estimated rotational barriers for both rings differ by about 5 kJ/mol. The ^{1}H NMR data for complexes **2** and **3** are given in Table II.

The rigid conformation of aromatic N substituents is obviously due to the presence of methyl groups on the dad fragment (biacetyl-derived ligands in **3a–c**). In the glyoxal-derived complexes **3f,g** normal NMR behavior is seen down to 220 K.

The cis and trans complexes **2** and **3** undergo reversible one-electron oxidations. The trans compounds are more easily oxidized than the cis compounds. The latter ones, however, show their oxidation wave in cyclic voltammograms in dichloromethane at more positive potentials than cis-$(bpy)_2RuCl_2$. In Table III half-wave potentials are given for the reversible oxidation, while cathodic peak potentials are listed for the irreversible first reduction.

For the ruthenium(II) complexes **2** and **3**, the chloro ligands are substitution inert even in the presence of silver tetrafluoroborate, but chloride is lost during the reduction. This opens a simple way into tris chelate complexes. Reduction of **2** or **3** with an alkali metal in the presence of dad, followed by subsequent reoxidation by iodine, gives $[(dad)_3Ru]^{2+}$, which is precipitated as the hexafluorophosphate salt **4**[12] (eq 1).

$$\underset{\textbf{2 or 3}}{(dad)_2RuCl_2} \xrightarrow[-2Cl^-]{+2e^-} \{(dad)_2Ru\} \xrightarrow{+dad} \{(dad)_3Ru\} \xrightarrow[-2I^-]{+I_2}$$

$$[(dad)_3Ru]^{2+} \xrightarrow{+NH_4PF_6} \underset{\textbf{4}}{[(dad)_3Ru](PF_6)_2} \quad (1)$$

Table III. Electrochemical Data of $Ru(dad)_2Cl_2$ Complexes (V) vs. $Ag/AgNO_3$ (0.1 M CH_3CN)[a]

compd	solvent	$E_{1/2}$(ox) (ΔE)[c]	E_{peak}(red)
2a	CH_2Cl_2[b]	−0.06 (66)	−1.67
3a	CH_2Cl_2	+0.22 (78)	−1.75
2b	CH_2Cl_2	−0.10 (76)	−1.71
	CH_3CN[b]	−0.19 (63)	−1.64, −1.80
3b	CH_2Cl_2	+0.13 (62)	−1.81
	CH_3CN	+0.09 (77)	−1.71, −1.75
2c	CH_2Cl_2	−0.15 (62)	−1.77
	CH_3CN	−0.19 (60)	−1.65, −1.86
3c	CH_2Cl_2	+0.16 (86)	−1.88
	CH_3CN	+0.10 (87)	−1.75, −1.80
2d	CH_2Cl_2	−0.06 (98)	−1.69
2e	CH_2Cl_2	+0.19 (78)	−1.29
2f	CH_2Cl_2	+0.20 (66)	−1.11
3f	CH_2Cl_2	+0.41 (64)	−1.20
	CH_3CN	+0.33 (63)	−1.28
bipy[d]	CH_2Cl_2	+0.05 (67)	−2.11

[a] Reference electrode potential is +0.3 V against SCE for CH_3CN solutions and +0.19 V for CH_2Cl_2 solutions (ferrocene pilot ion method). [b] 0.1 M $(n\text{-}Bu)_4N^+ClO_4^-$ as supporting electrolyte. [c] Values in parentheses $\Delta E_p = E_{p,ox} - E_{p,red}$ for the Ru(II)–Ru(III) couple; $E_{1/2}$(ox) calculated as the mean values of anodic and cathodic peak potentials from CV waves. Peak current ratios $i_{p,a}/i_{p,c}$ were between 1.0 and 0.96; E_p values did not change for scan rates tested between 50 and 200 mV/s; coulometry at constant potential gave n values of 1 ± 0.04; under the same conditions $[Ru(bpy)_3]^{2+}$ gave $n = 1$. [d] bipy = *cis*-$(bpy)_2RuCl_2$.

The formation of the cation $[(dad)_3Ru]^{2+}$ can also be detected, after the addition of dad, by cyclic voltammetry on the anodic scan. To achieve this, the reduction scan range has to be extended down to about −1.8 V, where a second irreversible reduction occurs.

We have not attempted to isolate the postulated ruthenium(0) intermediates $(dad)_3Ru$, but their existence has unequivocally been established by Poilblanc et al.[13]

We have shown that the barrier for trans–cis isomerization is quite high for ruthenium(II). The oxidized complexes are also stereochemically quite stable. No cis complexes can be detected after several redox cycles of trans Ru(II) ⇌ trans Ru(III). Addition of sodium naphthalene, on the other hand, gives a very fast, catalyzed, trans → cis isomerization. Less than 5% molar quantities of $Na^+Naphth^-$, added to the trans complex solutions at room temperature in THF, induce the characteristic trans → cis color change (eq 2).

$$trans\text{-}(dad)_2RuCl_2 \underset{-e^-}{\overset{+e^- \text{ (cat.)}}{\rightleftharpoons}} cis\text{-}(dad)_2RuCl_2 \qquad (2)$$

According to the CV results, the reaction (2) probably involves the initial loss of chloride with the subsequent uptake of the chloride after rearrangement and reoxidation.

Discussion

The substitution reaction of $Ru(C_6H_5C)_4Cl_2$ with dad favors the formation of trans complexes **2a–g** in a kinetically controlled reaction. Stereo models show that dad ligands, with aromatic N substituents tilted out of the dad coordination plane, are sterically less demanding than is 2,2′-bipyridine, because of the bpy hydrogen in the 6-position (Figure 4).

Steric bulk, on the other hand, is to be expected for the cis stereochemistry. Biacetyl-derived ligands **1a–d**, and the glyoxal-derived **1e**, cannot adopt an overall planar conformation. In Figure 5 a cis compound with C_2 symmetry is depicted viewed along the C_2 axis. From this picture of a special

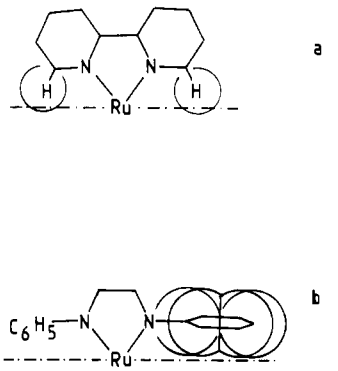

Figure 4. Comparison of a bpy–Ru and a dad–Ru fragment, with the *N*-phenyl substituent perpendicular to the chelate plane. For structure a, refer to ref 19, and for the dad–Ru chelate in b, refer to ref 17.

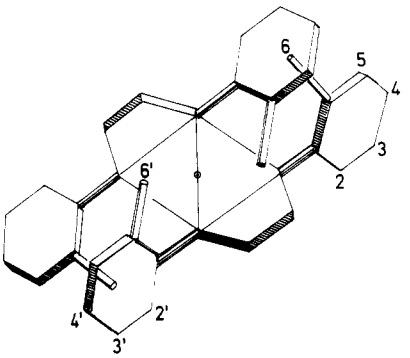

Figure 5. Stereo model of a cis bis chelate with aryl substituents perpendicular to the chelate plane (type 3 complex), viewed down the C_2 axis and showing the numbering scheme used in the text.

conformation, it is evident that one ortho proton (H6) is quite near to the center of another aromatic ring, which explains the shielding of this proton by aromatic-ring currents. There is no such influence for the corresponding ortho proton H2. The primed set of ortho protons is slightly shielded: H6′ by the dad double-bond anisotropy and H2′, considering conformations with dihedral (phenyl tilt) angles smaller than 90°, by the unprimed phenyl-ring current. It is also evident that ortho substituents larger than hydrogen cannot be accommodated in the 6 or 6′ position.

The anomalous ^1H NMR behavior of aromatic ortho protons has also been observed for complexes such as $[Fe(dad)_3]^{2+}$, for which an X-ray structural investigation[14] has confirmed the conformation deduced from the NMR results[15] ($\Theta_{av} \sim 75°$).

We have shown above that the NMR results prove the overall stereochemistry of the two complex types **2** and **3**. Also, the electron spectroscopic and electrochemical results for complexes **2** and **3** can easily be understood in terms of their different symmetry. As in all other cases of closed-shell dad metal complexes,[16] the electronic spectra in the visible region are dominated by an intense metal-to-ligand charge-transfer band. The three filled metal d orbitals (t_{2g} in O_h) transform as a,a,b in C_2 and as b_{1g},b_{2g},b_{3g} in D_{2h}. The lowest antibonding dad orbitals correspond to irreducible representations a,b in C_2 and b_{2g},b_{1u} in D_{2h}. Thus, all three d orbitals are stabilized by interactions of the back-bonding type in the cis complexes, with a parallel destabilization of dad LUMOs.[17] In the trans

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complexes, however, the d orbitals b_{1g},b_{3g} do not participate in back-bonding, nor is the π orbital b_{1u} affected.

We thus expect an easier oxidation and an easier reduction of trans complexes and, in the one-electron description of MO theory, a CT transition at lower energies as compared to cis complexes **3**. This is in good agreement with the experimental results. The reduction is indeed irreversible; these data should therefore be considered with caution.

The trans–cis isomerization barrier is not a direct function of steric hindrance. The conformational barriers of the N substituents are quite different for biacetyl- and glyoxal-derived complexes and lower than the configurational barriers in the case of N aromatic substituents. For N-aliphatic dad complexes, no trans isomers could be isolated so far; in boiling tetrahydrofuran only cis complexes are obtained from $Ru(C_6H_5CN)_4Cl_2$ and N-aliphatic dads. The most extreme conditions tested for the attempted trans–cis isomerization of *trans*-$[Ru(bpy)_2LL']^{2+}$ complexes are obviously much too mild for such a reaction.[8]

There is an interesting difference in the $(dad)_2RuCl_2$ cis–trans pairs compared to the cationic complexes $[(bpy)_2RuL_2]^{2+}$.[8] The latter ones show only small differences in their λ_{max} and $E_{1/2}(ox)$ values. For λ_{max} values, this can be explained by the fact that there are only two π^* orbitals of appropriate energy associated with two dad ligands, which are destabilized by d–π^* interactions. In the $(bpy)_2Ru^{II}$ case there is at least a manifold of six rather low π^* levels, to which CT transitions can occur. Therefore, their relative destabilization in the cis compounds (and hence stabilization of d orbitals) is smaller. However, the general trend with smaller relative excitation energies for the trans relative to the cis complexes is also found for the $(bpy)_2Ru$ complexes. The d $\rightarrow \pi^*$ CT energies of the cis compounds **3a–c** are practically the same as for $(bpy)_2RuCl_2$ (554 nm in CH_2Cl_2). The glyoxal-derived complexes **3f,g** have, in agreement with $(dad)Mo(CO)_4$ complexes,[16] lower energy π^* ligand orbitals and hence somewhat lower excitation energies, due to the replacement of the methyl groups by hydrogen. These spectral changes are much smaller than the effect of exchanging chloro ligands for O-, N- or P-containing ligands.[8]

From models, one can argue that the conformation of the aromatic substituents in biacetyl derivatives **2a–c** or **3a–c** is mainly determined by the biacetyl methyl groups. On the other hand, the conformation of the para-substituted glyoxal derivatives **2f,g** and **3f,g** is influenced by the coordination of the ligand to the metal, since the glyoxal ligands **1f,g** can adopt an overall planar geometry. The differences in the electronic spectral data for the complexes **2d** vs. **2a–c** (ca. 1100 cm^{-1}) and **2e** vs. **2f,g** (ca. 1250 cm^{-1}) indicate that these ortho substituents on the aromatic rings make the dihedral angle even greater than in complexes with meta- or para-substituted ligands. If the steric bulk in **2d,e** would prevent the ligands from coming as close to the metal as in the other trans complexes, then one would expect a smaller ligand field, a smaller d–π^* interaction, and thus a bathochromic shift. A hypsochromic shift of about 1100–1200 cm^{-1} is observed instead. In these complexes the dihedral angle of the 2,2′-substituted phenyl ring might be near 90°. The π^* orbitals relevant for the CT transition are thus localized in the small NCCN system instead of being delocalized, to some degree, in all the other complexes. The difference of about 250 mV observed in the oxidation potentials $E_{1/2}(ox)$ between the biacetyl complexes **2a–d** and the glyoxal complexes **2e,f** reflects the stronger donor character of the methyl-carrying ligands. In $(dad)Cr(CO)_4$ complexes with only one dad ligand, the complexes with the para-substituted ligands **1b,f** show an oxidation potential difference of about 120 mV, whereas the complexes with ortho-substituted ligands like **1d,e** show a difference of about 100 mV.[20] On the other hand, the oxidation of $(dad)Cr(CO)_4$ becomes much more difficult when going from $(\mathbf{1a})Cr(CO)_4$ or $(\mathbf{1b})Cr(CO)_4$ to complexes like $(\mathbf{1d})Cr(CO)_4$. The less bulky ligands obviously can follow the contraction due to M–N bond shortening upon oxidation. This relaxation is not possible for very bulky ligands and obviously very difficult for all of the $(dad)_2RuX_2$ complexes. Figure 4 indicates the rather close proximity between the aromatic groups in the "perpendicular" conformation.

Conclusions

We have prepared a series of new ruthenium(II) complexes with diazabutadienes (dad) ligands, which can be compared to complexes of 2,2′-bipyridine. Depending on the size of the N-substituents, the kinetically favored trans complexes can be isomerized to the more stable cis isomers. This allows one to study in detail the electronic and redox properties of ruthenium complexes with –N=C—C=N– ligand systems and to compare them with the important $[Ru(bpy)_3]^{2+}$ [18] and related $[Ru(bpy)_2(dad)]^{2+}$ complexes.[1]

The binding of dad to ruthenium(II) is sufficient to overcome the partial loss of conjugational energy (turning the phenyl rings out of the dad plane on going from planar glyoxal ligands **1f,g** to the trans complexes **2f,g** or cis complexes **3f,g**). In fact, there was only one prior, well-established, example of more than one, and hence noncoplanar, glyoxal bis(phenylimine) complexed to a metal in an octahedral complex.[13]

The electron spectroscopic data and the oxidation potentials show that the aromatic substituents in the trans complexes of type **2** face each other very closely and seem to adopt a cyclophane-like conformation in complexes **2d,e**. The desirable comparison of the complexes with N-aliphatic dad ligands of type **2** and **3** was, unfortunately, not possible because of the very fast isomerization of N-aliphatic trans complexes. Thermal reaction of $Ru(C_6H_5CN)_4Cl_2$ in boiling tetrahydrofuran with *N*-alkyl dad gives no trace of *trans*-$(N\text{-alkyl-dad})_2RuCl_2$, but does give the cis complex. Reduction of $RuCl_3 \cdot nH_2O$ with zinc at ambient temperature in the presence of Cy-N=CH—CH=N-Cy sometimes shows the expected blue trans complex (λ_{max} = 679 nm in THF), which isomerizes to the cis isomer (λ_{max} = 524 nm, isosbestic point at 601 nm) in a few minutes.

The difference in configurational stability between *N*-aryl and *N*-alkyl complexes of the type *trans*-$(dad)_2RuX_2$ is just opposite to the behavior of $(dad)M(CO)_4$ (M = Cr, Mo, W),[21] where the barriers of intramolecular cis–trans CO exchange for *N*-aryl dad is about 42–55 kJ/mol and >110 kJ/mol for *N*-alkyl dad. If the **2** → **3** isomerization goes via a trigonal-twist mechanism, then a strong steric interaction in the trigonal transition state could account for the high barrier. A bond-breaking mechanism is not taken into consideration because, even at temperatures as high as 160 °C, no exchange between free dad and coordinated dad or chloro ligands was observed.

The irreversibility of the electrochemical reduction of **2** or **3** does not independently allow for the confirmation of the conclusions drawn for the symmetry relationship and the conformational influence of the π^* levels. It does provide, however, a new method for mild substitution reactions of

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kinetically very inert ruthenium(II) halo complexes.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for providing the electrochemistry system and the Fonds der Chemischen Industrie for financial support. We also thank Degussa AG (Hanau), BASF AG (Ludwigshafen), and Hoechst AG (Frankfurt) for the donation of chemicals.

Registry No. **2a**, 90742-37-3; **2a**$^+$, 90742-46-4; **2b**, 90742-38-4; **2b**$^+$, 90742-47-5; **2c**, 90742-39-5; **2c**$^+$, 90742-48-6; **2d**, 90742-40-8; **2d**$^+$, 90742-49-7; **2e**, 90742-41-9; **2e**$^+$, 90742-50-0; **2f**, 90742-42-0; **2f**$^+$, 90742-51-1; **2g**, 90742-43-1; **3a**, 90821-16-2; **3a**$^+$, 90821-21-9; **3b**, 90821-17-3; **3b**$^+$, 90821-22-0; **3c**, 90821-18-4; **3c**$^+$, 90821-23-1; **3f**, 90821-19-5; **3f**$^+$, 90821-24-2; **3g**, 90821-20-8; **4**, 90742-45-3; $Ru(C_6H_5CN)_4Cl_2$, 21503-87-7.

Contribution from the Department of Chemistry and Ames Laboratory—U.S. DOE,[1] Iowa State University, Ames, Iowa 50011

Reactions of Aziridine, Oxirane, and Thiirane with Carbonyl and Thiocarbonyl Ligands in Complexes of Iron, Manganese, and Ruthenium: Syntheses of Cyclic Carbene Compounds

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Received August 1, 1983

The 3-membered heterocycles aziridine ($\overline{HNCH_2CH_2}$) and oxirane ($\overline{OCH_2CH_2}$) react with one CO group in each of the cationic carbonyl complexes $Cp(OC)_3Fe^+$, $Cp(OC)_3Ru^+$, $Cp(OC)_2(ON)Mn^+$, and $Cp(OC)_2(Ph_3P)Fe^+$ in the presence of a halide ion at 25 °C or below to form the corresponding 5-membered cyclic amino oxy $M{=}\overline{COCH_2CH_2NH}^+$ and dioxy $M{=}\overline{COCH_2CH_2O}^+$ carbene complexes (M = $Cp(OC)_2Fe$, $Cp(OC)_2Ru$, $Cp(OC)(ON)Mn$, $Cp(OC)(Ph_3P)Fe$). Aziridine and thiirane ($\overline{SCH_2CH_2}$) also react with the CS ligand in the mixed carbonyl thiocarbonyl complex $Cp(OC)_2(CS)Fe^+$ to give the corresponding aminothiocarbene ($M{=}\overline{CSCH_2CH_2NH}$) and dithiocarbene ($M{=}\overline{CSCH_2CH_2S}$) products. In the reactions $M{-}C{\equiv}Z^+ + \overline{YCH_2CH_2} \xrightarrow{X^-} M{=}\overline{CZCH_2CH_2Y}^+$ (Z = O, Y = NH and O; Z = S, Y = NH and S), the role of the halide ion X^- as a catalyst has been demonstrated. Prolonged reactions of oxirane with $Cp(OC)_2LM^+$ (M = Fe, L = CO; M = Mn, L = NO) in the presence of Br^- ion generate bis(dioxycarbene) derivatives $CpLM(\overline{COCH_2CH_2O})_2^+$. Mechanisms for these reactions have been proposed. Reactions of $Cp(OC)_2LM^+$ (M = Fe, L = CO; M = Mn, L = NO) with $[BrCH_2CH_2CH_2NH_3]Br$ and the bases azetidine ($\overline{HNCH_2CH_2CH_2}$) or oxirane and Br^- yield 6-membered amino-oxycarbene compounds $Cp(OC)LM(\overline{COCH_2CH_2CH_2NH})^+$. The basic behavior of oxiranes $R{-}\overline{CHCH_2O}$ in the presence of a halide catalyst is demonstrated by the isolation of the 5-membered dioxycarbene compound $Cp(CO)_2Fe(\overline{COCH_2CH_2O})^+$ from the reaction of $\overline{RCHCH_2O}$ with $Cp(OC)_3Fe^+$ in $BrCH_2CH_2OH$. IR and ^1H and ^{13}C NMR spectra of the compounds are discussed.

Introduction

There has been considerable interest in the reactions of the 3-membered heterocycles $\overline{YCH_2CH_2}$, where Y = NH (aziridine), O (oxirane), and S (thiirane), with transition-metal complexes. Simple coordination of aziridine through the N atom to metal ions has been observed.[3] One O-bonded oxirane compound, namely $[Cp(OC)_3Mo(\overline{OCH_2CH_2})]^+$, was also reported.[4] Aziridine and oxirane are also known to react with metal hydrido carbonyls[5,6] or with carbonyl anions[5,7] according to

$$LMH + \overline{YCH_2CH_2} \rightarrow LM{-}CH_2CH_2YH$$

LMH = $Co(CO)_4H$, $Mn(CO)_5H$, $CpMo(CO)_3H$, $CpW(CO)_3H$

$$LM^- + \overline{YCH_2CH_2} \rightarrow LM{-}CH_2CH_2Y^-$$

$LM^- = Co(CO)_4^-$, $CpFe(CO)_2^-$

Thiirane with hydrido carbonyls,[8,9] however, undergoes "desulfurization"

$$LMH + \overline{SCH_2CH_2} \rightarrow LM{-}SH + (LM)_2S + LM(SCH_2CH_2S)_2ML$$

In these and other reactions of metal carbonyl complexes,[4] the heterocycles $\overline{YCH_2CH_2}$ are observed to react at the metal centers. Recently, studies of the reactivity of CO ligands in metal carbonyl complexes have been stimulated by the search for catalytic reactions that convert CO into hydrocarbons, alcohols, and other organic products. Taking advantage of the tendency of highly strained 3-membered rings $\overline{YCH_2CH_2}$

(1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.
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