and disodiosilanes exhibit small calculated energy differences between planar and tetrahedral geometries for tetracoordinate silicon, as expected for what are essentially triple ion clusters.[23]

Conclusion

The lowest singlet and triplet potential energy surfaces for dilithiosilanes and disodiosilanes are very flat, as expected for effectively triple-ion clusters. Polarization at silicon, the hydridic character of the hydrogens (SiH_2), and, in the triplets, metal–metal bonding contribute to the existence of rather unusual structures.

Acknowledgment. We dedicate this paper to Professor Hans Bock on the occasion of his 60th birthday. This work was supported at Berkeley in part by AFOSR Grant 82-0114 and by NSF Grants CHE85-02137 and 87-21134 and at Erlangen by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and Convex Computer Corp. The Berkeley–Erlangen collaboration was also facilitated by a NATO grant. We thank A. J. Kos and J. A. Pople for preliminary calculations on this problem, A. E. Reed for discussions, and H. Xie for technical assistance.

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Notes

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NMR Investigation of the Rh_2^{4+} Complex $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ (form = *N,N'*-Di-*p*-tolylformamidinate) in the Presence of Phosphorus Donors. Evidence for the Interconversion from the Axial to Equatorial Adducts

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Received November 23, 1988

Complexes containing the Rh_2^{4+} core are of significance from the theoretical point of view as well as for their potential catalytic and carcinostatic activity.[1] Until recently the chemistry of this class of compounds has been limited to principally the presence of four carboxylate groups as bridge ligands while their reactivity with Lewis bases appeared to be restricted to the free axial sites. The substitution of the carboxylate groups by other bridging monoanionic ligands in the "lantern structure"[2] was shown to dramatically affect the redox potentials of these species but not their chemical reactivity, which is still restricted to the formation of axial adducts (class I according to the Andersen description).[3a] Recently, Drago et al. reported that the trifluoroacetate derivative $Rh_2(O_2CCF_3)_4$ reacts with nitrogen donor ligands such as *tert*-butyl isocyanide and pyridine giving 1:4 adducts.[4] In these adducts the neutral ligands are coordinated both axially and equatorially (class III) with the trifluoroacetate, exhibiting mono- and bidentate coordination. Furthermore, it was shown that the complexes $Rh_2(O_2CCF_3)_4L_2$ [L = PPh_3, $P(C_6H_{11})_3$], which belong to class I in the solid state, exist in solution as a mixture of axial and axial–equatorial adducts.[4b] Among the M_2(carboxylate)$_4$ (M = Rh, Mo) complexes, only the fluoroalkanecarboxylate-substituted systems lead to the formation of equatorial adducts. It thus appears that the formation of equatorial adducts is dependent on the presence of good leaving groups.

Recently we reported the synthesis of the Rh_2^{4+} complex $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ (form = *N,N'*-di-*p*-tolylformamidinate) in which the trifluoroacetate groups are in a position trans to the formamidinate ligands.[5] This should lead to the weakening of the Rh–O bond and enhance the chemical reactivity of the fluorocarboxylate groups. The reaction between the complex $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ and the phosphorus donors PPh_3, $P(C_6H_{11})_3$, $PMePh_2$, PMe_2Ph, $P(Bu^n)_3$, $P(Bu^t)_3$, $P(OMe)_3$, PPh_2H, and PMe_3 has now been investigated by NMR spectroscopy, and where possible the products were isolated.

Experimental Section

$Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ was prepared by the literature procedure.[5] The phosphorus ligands were all obtained from commercial suppliers and were used without further purification. Infrared spectra were recorded on KBr pellets with a Perkin-Elmer 783 instrument. The NMR spectra were measured in $CDCl_3$ by using a Bruker WP-80SY spectrometer for ^{19}F and some ^{31}P and a WH-400 spectrometer for ^{1}H, ^{13}C, ^{103}Rh, and some ^{31}P spectra. The chemical shifts are referenced to Me_4Si for ^{1}H and ^{13}C, $CFCl_3$ for ^{19}F, and external 85% H_3PO_4 for ^{31}P (high frequency is taken as being positive). Elemental analysis were performed by the Analytische Laboratorien Malissa and Reuter, Elbach, West Germany. All the reactions were carried out under nitrogen.

Synthesis of the Complexes $Rh_2(form)_2(O_2CCF_3)_2L$. The reactions were all carried out in a similar manner. The following procedure is typical. To a solution of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ (0.12 g, 0.13 mmol) in $CHCl_3$ was added the phosphorus ligand (mole ratio 1:1). The resultant solution was stirred for 30 min at room temperature. After this time, *n*-heptane was added, affording, by slow evaporation of the solvent, the monoadducts.

L = PPh_3. Red crystals formed, yield 80%. Anal. Calcd for $Rh_2C_{52}H_{45}N_4O_4F_6P$: C, 54.75; H, 3.97; N, 4.91; P, 2.71. Found: C, 54.95; H, 4.11; N, 4.93; P, 2.70. Infrared spectrum (KBr pellet, cm^{-1}): $\nu_{asym}(CO_2)$ 1635 (s); ν(N=C=N) 1570 (s). ^{103}Rh NMR ($CDCl_3$): δ 3394 (dd), 7086 (d, J_{Rh-Rh} = 38.6 Hz).

L = $P(C_6H_{11})_3$. Red crystals formed, yield 85%. Anal. Calcd for $Rh_2C_{52}H_{63}N_4O_4F_6P$: C, 53.89; H, 5.48; N, 4.83; P, 2.67. Found: C, 54.14; H, 5.39; N, 4.85; P, 2.75. Infrared spectrum (KBr pellet, cm^{-1}): $\nu_{asym}(CO_2)$ 1640 (s); ν(N=C=N) 1570 (s). ^{13}C NMR ($CDCl_3$): δ 34.1 (d, CH, J_{P-C} = 18 Hz), 29.0 (s, CH_2), 27.4 (d, CH_2, J_{P-C} = 9 Hz), 26.1 (s, CH_2), 114.4 (s, CF_3), 112.9 (s, CF_3), 147.1, 125.4, 130, and 134.1 (ipso, ortho, meta, and para carbons), 147, 124.7, 129.7, and 134.1 (ipso, ortho, meta, and para carbons), 146.2, 123.7, 129.2, and 133.2 (ipso, ortho, meta, and para carbons), 146, 122.6, 129, and 133 (ipso, ortho, meta, and para carbons), 171.3 (s, CO_2), 168.8 (s, CO_2).

L = $P(Bu^t)_3$. Green crystals formed, yield 85%. Anal. Calcd for $Rh_2C_{46}H_{59}N_4O_5F_6P$: C, 50.28; H, 5.41; N, 5.09; P, 2.81. Found: C, 49.46; H, 5.14; N, 4.96; P, 3.85. Infrared spectrum (KBr pellet, cm^{-1}): $\nu_{asym}(CO_2)$ 1660 (s); ν(N=C=N) 1575 (s).

L = $P(Bu^n)_3$. Dichroic green-red crystals formed, yield 75%. Anal. Calcd for $Rh_2C_{46}H_{57}N_4O_4F_6P$: C, 51.12; H, 5.31; N, 5.18; P, 2.86. Found: C, 51.38; H, 5.38; N, 5.09; P, 2.90. Infrared spectrum (KBr pellet, cm^{-1}): $\nu_{asym}(CO_2)$ 1660 (s); ν(N=C=N) 1570 (s). ^{1}H NMR ($CDCl_3$): δ 0.71 (d, PCH_3, J_{P-H} = 10 Hz). ^{13}C NMR ($CDCl_3$): δ 25.6 (d, CH_2, J_{P-C} = 7 Hz), 24.6 (d, J_{P-C} = 10 Hz), 20.8 (d, J_{P-C} = 7 Hz), 13.4 (s, CH_3), 112.9 (s, CF_3), 151.3, 126.5, 129.5, and 134.4 (ipso, ortho,

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Table I. ^{31}P and ^{19}F Chemical Shifts (ppm) and Coupling Constants (Hz) for $Rh_2(form)_2(O_2CCF_3)_2L$ in $CDCl_3$

L	structure	temp, K	$\delta(^{31}P)$	$^1J_{Rh-P}$	$^2J_{Rh-P}$	$\delta(^{19}F)$ (308 K)	
PPh_3	I	225	−35.8	84.8	56.7		
	II	308	27.8	138.0	6.3	−74.8	−76.3
$P(C_6H_{11})_3$	I	225	−34.0	83.0	62.0		
	II	308	20.2	133.0	6.0	−75.2	−76.1
$P(Bu^n)_3$	I	225	−45.1	99.8	50.1	−75.5	
	II	308	19.0	135.7	6.3	−75.1	−76.2
$PMePh_2$	I	225	21.05	89.0	59.2		
	II	225	−51.78	135	7		
	I	308	20.75	91.5	61.3		
	II	308	−54.17	135	6.8		
PPh_2H	I	225	−36.6	101.1	55.3		
PMe_2Ph	I	225	−51.4	99.9	52.3		
	I	308	−54.5	100.2	55.9		
	II	308	16.0	136.8	6.0	−74.9	−76.1
$P(OMe)_3$	I	225	23.5	154.3	84.1		
	I	308	20.3	155.6	88.6		
PMe_3	I	225	−56.3	104.3	50.6		
	I	308	−60	104.7	53.89		

meta, and para carbons), 147.1, 123.3, 129.3, and 132.9 (ipso, ortho, meta, and para carbons), 170.1 (s, CO_2).

L = PMe_2Ph. Green crystals formed, yield 85%. Anal. Calcd for $Rh_2C_{42}H_{41}N_4O_4F_6P$: C, 54.38; H, 4.45; N, 6.03; P, 3.33. Found: C, 54.89; H, 4.48; N, 6.31; P, 3.1. Infrared spectrum (KBr pellet, cm^{-1}): $\nu_{asym}(CO_2)$ 1655 (s); $\nu(N{=}C{=}N)$ 1570 (s). ^1H NMR ($CDCl_3$): δ 0.71 (d, PCH_3, J_{P-H} = 10 Hz). ^{13}C NMR ($CDCl_3$): δ 9.3 (d, PCH_3, J_{P-C} = 9.3 Hz), 112.8 (s, CF_3), 151.4, 126.7, 129.7, and 134.8 (ipso, ortho, meta, and para carbons), 146.9, 123.3, 129.4, and 133 (ipso, ortho, meta, and para carbons), 170.2 (s, CO_2).

NMR Tube Reactions. These reactions were carried out in a similar manner. The following procedure is typical. Two different samples of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ (0.04 g, 0.043 mmol) were dissolved in $CDCl_3$ (1 mL) under nitrogen, and the solutions were cooled to 225 K. The solutions were then transferred under nitrogen in 10-mm NMR tubes cooled at 225 K. The phosphorus ligand dissolved in $CDCl_3$ was cooled at 225 K and then added by syringe to each sample in molar ratios of 1:1 and 1:2, respectively. After the ^{31}P NMR spectra had been recorded the solutions were warmed to 308 K and the spectra recorded again. The samples were left standing in the tubes for 2 days at room temperature, and no changes were observed in the ^{31}P NMR spectra of the PPh_3, $P(C_6H_{11})_3$, $P(Bu^t)_3$, $P(Bu^n)_3$, $PMePh_2$, PMe_2Ph, and PMe_3 adducts, while the spectra of the $P(OMe)_3$ and PPh_2H derivatives were largely different, suggesting dimer decomposition.

Results and Discussion

Generation and Spectral Characterization of the Complexes. The phosphine derivatives $Rh_2(form)_2(O_2CCF_3)_2L$ (L = PPh_3, $P(C_6H_{11})_3$, $P(Bu^t)_3$, $P(Bu^n)_3$, $PMePh_2$, PPh_2H, PMe_2Ph, $P(OMe)_3$, PMe_3) have been generated in a ^{31}P NMR tube by adding, via syringe, 1 equiv of the appropriate phosphine to a $CDCl_3$ solution of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ at 225 K. The reactions have been also performed with different complex/phosphorus ligand ratio. The PPh_3, $P(Cy)_3$, $P(Bu^t)_3$, $P(Bu^n)_3$, and PMe_2Ph derivatives have been isolated and characterized by elemental analysis, IR, and NMR spectroscopy.

The ^{31}P NMR spectrum (Figure 1) recorded at 225 K reveals the quantitative formation of 1:1 adducts. In each case, when the phosphorus ligand is added, an isomer is formed that shows a doublet of doublets resonance with two large coupling constants of 80–156 and 50–89 Hz (Table I). This is consistent with the formation of an isomer (class I) with a linear axial arrangement of Rh–Rh–P. On warming to room temperature, the PMe_2Ph, PPh_2Me, PPh_3, PBu^n_3, and $P(C_6H_{11})_3$ adducts isomerize to give a second species, while the spectra of the $P(OMe)_3$, PPh_2H, and PMe_3 adducts were insignificantly changed. The reaction of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ with the very bulky PBu^t_3 was also monitored by ^{31}P NMR spectroscopy. In this case only broad signals were obtained at low and room temperature, suggesting the occurrence of exchange phenomena. The lability of the $P(Bu^t)_3$ derivative relative to the other phosphorus ligands is no doubt steric in origin. The extent of isomerization follows the bulk of the ligand; it is virtually 100% for L = PPh_3 and PCy_3, 17% for L = PMe_2Ph, 34% for L = $P(Bu^n)_3$, and 72% for L = $PMePh_2$. The ^{31}P NMR spectrum of the second isomer still exhibits the X part of an AMX pattern as a doublet of doublets and is characterized by a shift of the ^{31}P chemical shift ca. 60 ppm to higher frequency with coupling constants to ^{103}Rh of ca. 135 and 6 Hz. These coupling constants are consistent with the formation of equatorial adducts with a bent arrangement of Rh–Rh–P (class II). The chemical shifts and J_{P-Rh} couplings compare well with those found

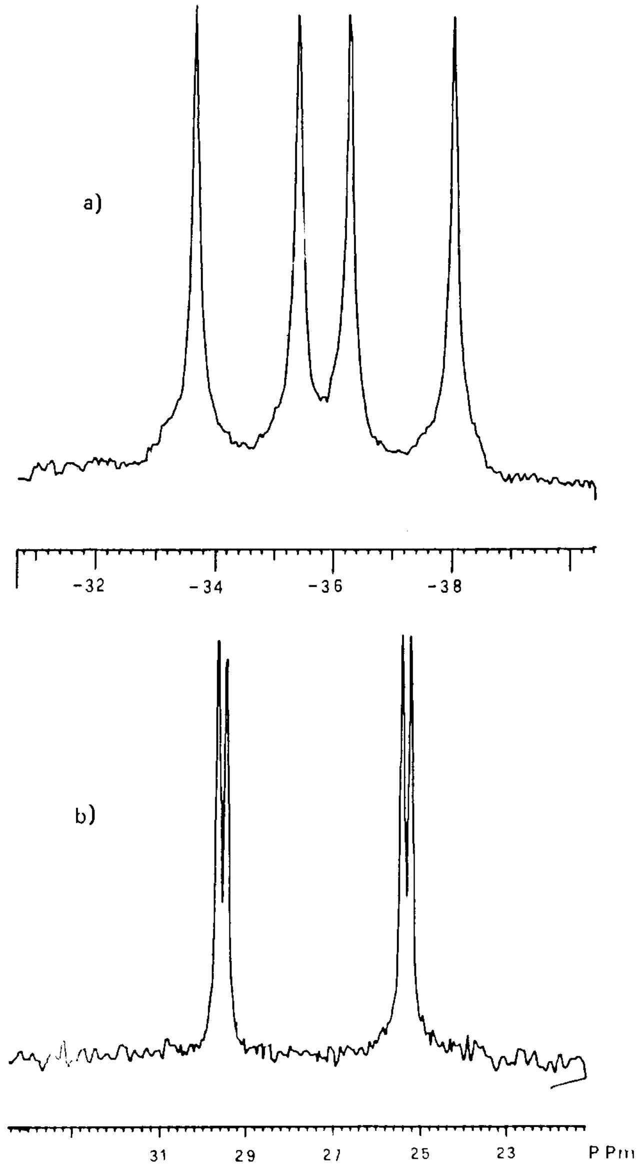
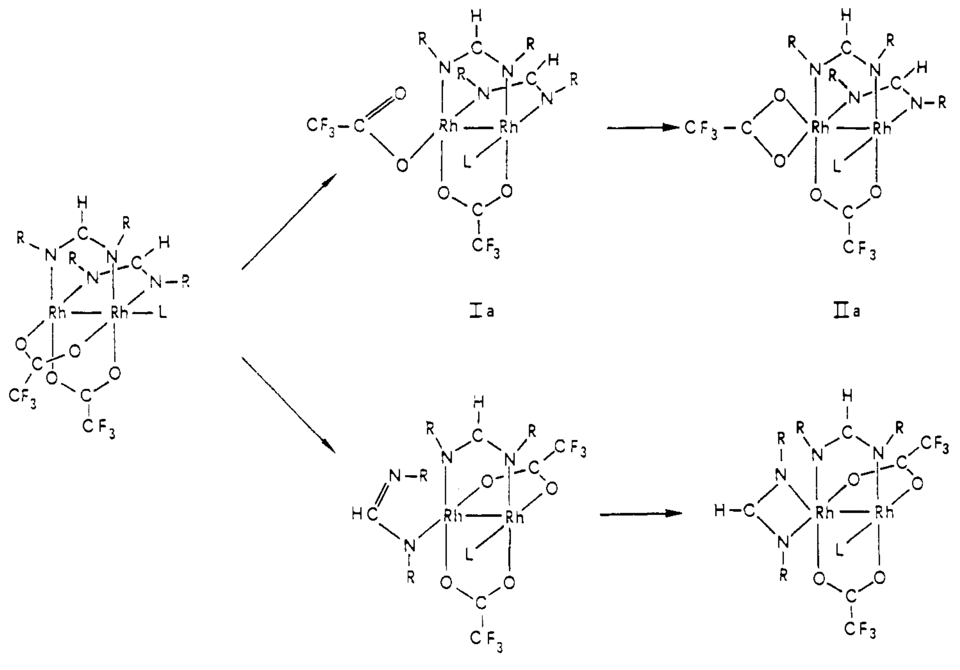


Figure 1. ^{31}P NMR spectra of $Rh_2(form)_2(O_2CCF_3)_2PPh_3$ in $CDCl_3$: (a) at 225 K; (b) at 308 K.

Scheme I



in $Rh_2(O_2CCF_3)_4L_2$ [L = PPh_3, $P(C_6H_{11})_3$] and in the asymmetric Rh_2^{4+} complex $Rh_2(form)_3(NO_3)(PPh_3)$.[6] The smaller $^{1}J_{Rh-P}$ coupling in the axial isomer relative to the equatorial is very likely due to the well-known trans effect operating along the Rh–Rh bond and is in keeping with the increasing of the Rh–P bond distances observed on going from Rh–P(equatorial)[7] to Rh–P(axial).[1]

The conversion of the linear to the bent form for the PPh_3 and PCy_3 adducts is irreversible; upon cooling of the sample to 225 K, ^{31}P NMR spectroscopy shows that the bent isomer does not transform back to the linear form. Similarly, the extent of isomerization in the $P(Bu^n)_3$, PMe_2Ph, and $PMePh_2$ derivatives is not affected when the room-temperature solution is cooled to 225 K. When the mixtures are left standing for 2 days, no change in the isomer distribution is seen.

The stability of the monoadducts (class I) appears strongly dependent on the bulk of the phosphorus ligands used. It is worthwhile mentioning that in the parent complex the values of the Rh–Rh–O(axial) angles [167.9 (1) and 169.3 (1)°] deviate significantly from linearity while in the tetrakis(trifluoroacetate) derivative the same angles are 178.7 (7)°.[8] The reason for this has been ascribed to steric interactions between the water molecules and the tolyl groups. The steric overcrowding of the *p*-tolyl groups and the substituents on the phosphorus atoms very likely determine the stability of the axial monoadducts. In our opinion the same explanation cannot be invoked for the formation of the equatorial adducts (class III) $Rh_2(O_2CCF_3)_4L_2$ (L = PPh_3, PCy_3), since the Rh–Rh–O(axial) angles are almost linear and no significant steric interactions between the trifluoroacetate and phosphorus ligands can be postulated. On the other hand, the analogous Mo derivative $Mo(O_2CCF_3)_4$ forms equatorial adducts (class II) with small P donors such as PMe_3, PMe_2Ph, and PEt_3 and axial adducts with large phosphines.[3]

In the PPh_3 derivative the inequivalence of the two rhodium atoms was proved by the ^{103}Rh NMR spectrum, which shows two resonances at δ 3394 (dd) and 7086 (d). These chemical shifts lie in the range quoted for this class of compounds (3000–8000).[6,9,10] The J_{Rh-Rh} coupling constant of 38.6 Hz, although quite different from the values of ca. 8 Hz reported in the Rh_2^{4+} derivatives with nonpolar Rh–Rh bond,[4b,9] compares well with those found in the asymmetric complexes $[Rh_2(mhp)_4]_2$ (mhp = 6-methyl-2-hydroxypyridinate) (34 Hz)[10] and $Rh_2(form)_3(NO_3)(PPh_3)$ (34 Hz).[6]

Table II. ^{1}H and ^{13}C Chemical Shifts (ppm) for $Rh_2(form)_2(O_2CCF_3)_2L$ in $CDCl_3$ at 308 K

L	$\delta(^{1}H)$		$\delta(^{13}C)$	
	NCHN	CH_3	NCHN	CH_3
PMe_2Ph	*a*	2.21	168.2	21.0
		2.23		20.4
		2.07		
		2.20		
		2.24		
		2.29		
$P(C_6H_{11})_3$	7.88 dt[b]	2.17	169.3	20.9
	7.53 dd[c]	2.18	163.1	20.9
		2.28		20.8
		2.34		20.6
$P(Bu^n)_3$	7.34 m	2.21	168.4	20.7
		2.26		20.8
	7.37 t[d]	2.23		
	7.50 dd[e]	2.26		
		2.31		
		a		

[a] Signal is obscured. [b] Doublet of 8 Hz; triplet of 3 Hz. [c] Doublet of doublets of 3.5 and 5 Hz. [d] Triplet of 4 Hz. [e] Doublet of doublets of 3.5 and 5 Hz.

The isomerization of the linear to the bent complex occurs presumably through ring opening of one Rh–O–C–O–Rh fragment according to Scheme I.

An alternative mechanism that involves ring opening of the Rh–N–C–N–Rh fragment and formation of the bent isomer IIb cannot be ruled out.

In order to shed more light on the structure of the bent isomer, ^{1}H, ^{13}C, and ^{19}F NMR spectra of the PMe_2Ph, PBu^n_3, and $P(C_6H_{11})_3$ derivatives were examined in more detail at room temperature. These derivatives were chosen as the ratio of the two isomers lies predominantly in favor of the linear Rh–Rh–P isomer for the PMe_2Ph derivative and exclusively in favor of the bent

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Rh–Rh–P isomer for the $P(C_6H_{11})_3$ derivative. The $PBu^n{}_3$ derivative consists of predominantly the linear Rh–Rh–P isomer, but there are significant quantities of the bent isomer present. The ^{19}F NMR spectra (Table I) show only one signal for the linear isomer but two for the bent isomer. In the ^1H and ^{13}C NMR spectra the linear isomers show only one type of formamidinate ligand, with inequivalent *p*-tolyl groups, but the equatorial adduct shows that both the formamidinate ligands are inequivalent. The ends of the formamidinate ligands are also inequivalent, giving rise to four sets of signals due to *p*-tolyl groups (Table II). Furthermore, the IR spectra show, beside the bands associated with the formamidinate fragments, one strong band in the range 1660–1630 cm^{-1} easily attributed to ν_{asym}(O–C–O). In each case no stretching frequencies due to monodentate trifluoroacetate groups are present. Although the spectral data do not allow an unambiguous assignment of the structure of the equatorial adducts, we nevertheless suggest structure IIa for the bent isomer, since (a) structure IIb is more sterically congested than IIa and (b) it would involve breaking of the Rh–N–C–N–Rh fragment, which has been shown to be very stable while the trifluoroacetate group is known as a good leaving group. The isomerization reported here is quite uncommon for this class of compounds, but there is some precedence for these transformations. In fact, although not directly observed, such isomerism must be operating when the axial phosphine derivatives $Rh_2(O_2CCH_3)_4L_2$ ($L = PPh_3$,[11] P(*o*-$ClC_6H_4)Ph_2$[7b]) undergo thermal ortho-metalation reactions leading to complexes where the ortho-metalated phosphine acts as a bridging ligand. Furthermore, the complex $Mo_2(O_2CCF_3)_4$ reacts with $PMePh_2$, giving class I[3b] at room temperature or class II[12] adducts under more strenuous experimental conditions.

Acknowledgment. We thank the Public Ministry of Education for financial support.

Registry No. $Rh_2(form)_2(O_2CCF_3)_2(OH_2)_2$, 105164-41-8; $Rh_2(form)_2(O_2CCF_3)_2(PPh_3)$ (axial isomer), 121288-94-6; $Rh_2(form)_2(O_2CCF_3)_2(PPh_3)$ (equatorial isomer), 121289-06-3; $Rh_2(form)_2(O_2CCF_3)_2(P(C_6H_{11})_3)$ (axial isomer), 121288-95-7; $Rh_2(form)_2(O_2CCF_3)_2(P(C_6H_{11})_3)$ (equatorial isomer), 121288-96-8; $Rh_2(form)_2(O_2CCF_3)_2(P(Bu^n)_3)$ (axial isomer), 121288-97-9; $Rh_2(form)_2(O_2CCF_3)_2(P(Bu^n)_3)$ (equatorial isomer), 121288-98-0; $Rh_2(form)_2(O_2CCF_3)_2(PMePh_2)$ (axial isomer), 121288-99-1; $Rh_2(form)_2(O_2CCF_3)_2(PMePh_2)$ (equatorial isomer), 121289-00-7; $Rh_2(form)_2(O_2CCF_3)_2(PPh_2H)$, 121289-01-8; $Rh_2(form)_2(O_2CCF_3)_2(PMe_2Ph)$ (axial isomer), 121289-02-9; $Rh_2(form)_2(O_2CCF_3)_2(PMe_2Ph)$ (equatorial isomer), 121289-03-0; $Rh_2(form)_2(O_2CCF_3)_2(P(OMe)_3)$, 121289-04-1; $Rh_2(form)_2(O_2CCF_3)_2(PMe_3)$, 121289-05-2; $Rh_2(form)_2(O_2CCF_3)_2(P(Bu^t)_3)$, 121289-07-4; Rh, 7440-16-6.

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Isolation and Identification of a *trans*-Bis(bipyridine) Complex of Rhodium(III). Crystal Structure of [*trans*-$Rh(bpy)_2(Cl)]_2(H_5O_3)(ClO_4)_3$: Evidence for a H_5O_3 Bridging Group

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Received August 10, 1988

The trans configuration of complexes of the type $M(bpy)_2XY^{n+}$ (bpy = 2,2′-bipyridine) has long been considered as rather improbable due to the steric hindrance caused by the α-protons in such structures.[1] In the case of bis(bipyridine) complexes of d^8 metal ions (Pd(II), Pt(II)), the steric strain is relieved by structural modifications.[2] In light of these trends it is quite understandable that thermal and photochemical aquation reactions of *cis*-$Rh(bpy)_2Cl_2^+$ were reported to proceed stereoretentively.[3] However, our high-pressure mechanistic studies of the photoaquation of this complex first[4] revealed some indirect and later[5] direct evidence for the formation of *trans*-$Rh(bpy)_2Cl_2^+$ and *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$. It follows that bis(bipyridine) complexes of Rh(III) can exhibit a similar cis–trans isomerization as found for related Ru(II) complexes before.[6] The configurational differences in the case of the title compound show up very well in the RhN_4XY^{n+} skeletal vibrations as they do in other cases with amine ligands. This is also demonstrated here for *cis*- and *trans*-$Rh(bpy)_2XY^{n+}$ (X, Y = H_2O or Cl$^-$). In the meantime we have succeeded in growing crystals of *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ (as the perchlorate salt) suitable for a structure determination. The results reported here not only underline the validity of our earlier conclusions but also reveal a fascinating $H_5O_3^-$ bridging group linking two $Rh(bpy)_2Cl^{2+}$ units in the solid state.

Table I. Crystal Data and Data Collection Parameters for $[Cl(bpy)_2Rh{-}H_5O_3{-}Rh(bpy)_2Cl](ClO_4)_3$

formula	$Rh_2C_{40}H_{37}N_8Cl_5O_{15}$	space group	$P\bar{1}$ (No. 2)
fw	1252.85	μ(Mo Kα), cm^{-1}	10.7
cell params		D_{calcd}, g cm^{-3}	1.81
a, Å	12.861 (2)	D_{obsd}, g cm^{-3}	1.80
b, Å	13.069 (1)	T, °C	25
c, Å	16.046 (5)	radiation	Mo Kα (0.7107 Å, graphite monochromator)
α, deg	63.58 (2)		
β, deg	73.80 (2)		
γ, deg	73.15 (1)	$R(F_o)$	0.043
V, Å^3	2293.05	$R_w(F_o)$	0.046
Z	2		

Experimental Section

The cis and trans complexes discussed in this paper were prepared and characterized as described elsewhere.[5] Crystals of *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ suitable for X-ray analysis were grown from a neutral aqueous solution of this complex. The light yellow compound, which may be formulated as $[Cl(bpy)_2Rh{-}H_5O_3{-}Rh(bpy)_2Cl](ClO_4)_3$, crystallizes in the triclinic space group $P\bar{1}$ or $P1$. Statistical analysis of the intensities led to the former centrosymmetric space group, and the subsequent successful solution and refinement of the structure confirmed this choice. The crystal and refinement data are given in Table I. The X-ray crystallographic data were obtained on a Enraf-Nonius CAD 4F diffractometer using graphite-monochromated Mo Kα radiation. No decomposition of the crystal was detected during the data collection. The data were corrected for Lorentz–polarization and absorption effects.

The structure was solved by means of Patterson and Fourier methods. All the calculations were done on a Univac 1100 computer using the X-ray 72 system of programs. The final R value was 0.043, with use of anisotropic thermal parameters for all the non-hydrogen atoms. The atomic coordinates are given in Table II.

Infrared spectra were recorded on a Nicolet 5 SX FT-IR instrument (4000–400 cm^{-1}, KBr disk) and on a Perkin-Elmer 325 grating spectrophotometer (400–200 cm^{-1}, CsI disk).

Results and Discussion

Crystal Structure. The crystal is composed of discrete $Cl(bpy)_2Rh{-}H_5O_3{-}Rh(bpy)_2Cl^{3+}$ cations and ClO_4^- anions. The most important bond lengths and angles are given in Table III. Figure 1 shows the numbering system of the atoms in the Rh(III) complex. There are two crystallographically independent *trans*-$Rh(bpy)_2Cl^{2+}$ units linked by a $H_5O_3^-$ bridge to form the trans dimer. The 3+ charge of the dimeric unit is balanced by three perchlorate ions in the crystal. The bond distances and angles

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