Inorg. Chem. **1980,** *19,* 3343–3351

Contribution from the Anorganisch Chemisch Laboratorium, J. H. van't Hoff Instituut,
University of Amsterdam, 1018 WV Amsterdam, The Netherlands

σ^2-N′,μ^2-N,η^2-C=N Coordination as the Activating Step in the Carbon–Carbon Bond Formation between Two α-Diimines in Dinuclear Ruthenium Carbonyl Complexes. X-ray Structure of Tetracarbonylbis[glyoxal bis(isopropylimine)]diruthenium[1]

L. H. STAAL,[2] L. H. POLM,[2] R. W. BALK,[2] G. VAN KOTEN,[2] K. VRIEZE,*[2] and A. M. F. BROUWERS[3]

Received January 31, 1980

$Ru_3(CO)_{12}$ and 1,4-diazabutadiene ligands (DAB) react to form the binuclear complexes $Ru_2(CO)_6$(DAB), $Ru_2(CO)_5$(IAE) (IAE = bis[(alkylimino)(alkylamino)ethane]), $Ru_2(CO)_4$(IAE), and $Ru_2(CO)_4(DAB)_2$. In $Ru_2(CO)_6$(DAB) the DAB ligand is coordinated via two lone pairs and one pair of π electrons. The η^2 coordination is responsible for the activation of the π system with respect to C–C bond formation, resulting in coupling of two DAB ligands into the 10-e-donating IAE ligand. Monitoring the reaction carefully with IR spectroscopy, $Ru_2(CO)_5$(IAE) complexes could be isolated which contain a bridging carbonyl group. Refluxing at 120 °C for a longer period (4 h or more) resulted in the subsequent reaction product $Ru_2(CO)_4$(IAE), in which the bridging carbonyl is lost, under simultaneous Ru–Ru bond formation. After prolonged heating at 150 °C of $Ru_2(CO)_4$(IAE) in solution, $Ru_2(CO)_4(DAB)_2$ was obtained. In these complexes the C–C bond in the IAE ligand, holding together the two DAB fragments, was broken, which was proven by an X-ray structure determination. Crystals of $Ru_2(CO)_4$[glyoxal bis(isopropylimine)]$_2$ are monoclinic with space group $C2/c$ and cell constants a = 17.274 (1) Å, b = 10.468 (1) Å, c = 14.386 (1) Å, β = 108.864 (4)°, and Z = 4. The molecule contains two DAB ligands coordinated in σ^2-N′,μ^2-N,η^2-C=N mode, with C–N distances of 1.30 (1) and 1.43 (1) Å for the σ^2-N′ and the μ^2-N,η^2-C=N coordinated imine fragments, respectively. The spectroscopic properties of all complexes have been measured (^{1}H NMR, IR, UV spectroscopy) and have been compared with the results for $Fe_2(CO)_6$(DAB). The complexes have also been characterized by mass spectroscopy and gave the isotope distribution which is characteristic for binuclear ruthenium complexes.

Introduction

The coordination properties of 1,4-diazabutadienes (DAB or α-diimines)[4] in metal carbonyl chemistry have been the subject of many extensive investigations. Coordination via the lone pairs on nitrogen, which is the symmetry-forced coordination mode, has been found in most of the metal carbonyl DAB complexes: $M(CO)_4$(DAB) (M = Cr, Mo, W),[5-8] $M(CO)_3X$(DAB) (M = Mn, Re; X = Cl, Br, I),[9] Mn$(CO)_5M(CO)_3$(DAB) (M = Mn, Re),[10] $Fe(CO)_3$(DAB),[11-13] and $Ni(CO)_2$(DAB).[14,15]

Besides coordination via the lone pairs only (σ,σ coordination), a few examples are known for a coordination mode in which one pair of π electrons of the N=C—C=N skeleton is also involved in the metal–ligand bonding, i.e., σ^2-N′,μ^2-N,η^2-C=N coordination. For reasons of conciseness this mode will be called "σ,π coordination" (which in principle is an incorrect term, since it could refer to the 4e σ,π coordination, which, however, has not been observed as yet).[13] Recently we succeeded in the synthesis of $MCo(CO)_6$(DAB) (M = Mn, Re), which complexes give important information about the role of substitutents on the imine positions of the DAB ligand with respect to the π-bonding ability of the C=N fragments.[16] The μ^2-N,η^2-C=N coordination only occurred for (H)C=N fragments, while (CH_3)C=N fragments were always found in the σ^2-N′ coordination mode.

The ability to π coordinate is an important factor in the reactivity of DAB ligands in metal carbonyl complexes. The first example of a reaction between two coordinated DAB ligands was reported for $Mo_2(CO)_6$(IAE) (IAE = bis[(alkylimino)(alkylamino)ethane].[17] In these complexes a C–C bond was formed between two DAB ligands after oxidative elimination of a carbonyl group from $[Mo(CO)_4(DAB)]^-$. The reaction of the ligands on the metal carbonyl units is shown schematically in Figure 1.

In the proposed mechanism for the IAE formation in $Mo_2(CO)_6(IAE)$[17] we assumed that carbon–carbon bond formation occurred in a short-living intermediate containing "σ,π coordinated" DAB ligands. In this paper we will provide further evidence that "σ,π coordination" of the DAB ligands is indeed a prerequisite for the formation of IAE ligands in binuclear ruthenium carbonyl complexes.

Experimental Section

^{1}H NMR spectra were recorded on a Varian T60 and a Varian XL-100 apparatus, IR spectra were obtained with a Perkin-Elmer 283 infrared spectrophotometer, UV–visible measurements were carried out by using a Cary 14 spectrophotometer, and mass spectra were recorded with a Varian MAT 711.

All preparations were carried out in an atmosphere of purified nitrogen, by using solvents that were carefully dried and distilled before use.

The ligands have been prepared according to standard procedures.[8] $Ru_3(CO)_{12}$ and $Fe(CO)_5$ were purchased from Strem Chemicals and used without purification. $Fe_2(CO)_9$ was prepared photochemically from $Fe(CO)_5$.

Preparations of $Ru_2(CO)_6$(DAB) [DAB = Glyoxal Bis(*tert*-butylimine), Glyoxal Bis(isopropylimine), Glyoxal Bis(cyclohexylimine), Methylglyoxal Bis(isopropylimine)]. $Ru_3(CO)_{12}$ (0.33 mmol) and DAB

---

(1) Binuclear Metal Carbonyl Complexes. 4. For part 3 see: L. H. Staal, L. H. Polm, G. van Koten, and K. Vrieze, *Inorg. Chim. Acta*, **37**, L 485 (1979).

(2) Anorganisch Chemisch Laboratorium.

(3) Laboratorium voor Kristallografie.

(4) The names used for the ligands are derived from the related diketones glyoxal or methylglyoxal. The abbreviation DAB is referring to 1,4-diazabutadiene. Instead of the name derived from the diketone, sometimes the name 1,4-dialkyl(aryl)-1,4-diazabutadiene is used in the literature. We have adapted ourselves to the more commonly used nomenclature for the α-diimines.

(5) L. H. Staal, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, **26**, 255 (1978).

(6) L. H. Staal, A. Terpstra, and D. J. Stufkens, *Inorg. Chim. Acta*, **34**, 97 (1979).

(7) R. W. Balk, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, **28**, 133 (1978).

(8) H. Bock and H. tom Dieck, *Chem. Ber.*, **100**, 228 (1967).

(9) L. H. Staal, A. Oskam, and K. Vrieze, *J. Organomet. Chem.*, **170**, 235 (1979).

(10) L. H. Staal, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, **175**, 73 (1979).

(11) S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, **6**, 20 (1967).

(12) H. tom Dieck and A. Orlopp, *Angew. Chem.*, **87**, 241 (1975).

(13) L. H. Staal, L. H. Polm, and K. Vrieze, *Inorg. Chim. Acta*, **40**, 165 (1980).

(14) H. tom Dieck and H. Bock, *Angew. Chem.*, **78**, 549 (1966).

(15) H. D. Hausen and K. Krogmann, *Z. Anorg. Allg. Chem.*, **389**, 247 (1972).

(16) (a) L. H. Staal, J. Keijsper, L. H. Polm, and K. Vrieze, *Inorg. Chim. Acta*, in press; (b) L. H. Staal, J. Keijsper, G. van Koten, K. Vrieze, J. A. Gras, and W. P. Bosman, *Inorg. Chem.*, in press.

(17) L. H. Staal, A. Oskam, K. Vrieze, E. Roosendaal, and H. Schenk, *Inorg. Chem.*, **18**, 1634 (1979).

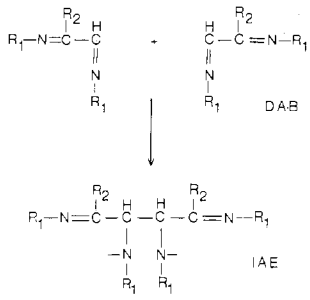

Figure 1. Schematic formation of IAE from two DAB ligands.

(0.50 mmol) were stirred for 3 h in 40 mL of *n*-heptane at 90 °C. Directly after the reaction was started, an intensely colored red solution was found, which was extremely air sensitive. Gradually the solution became yellow-orange, and the reaction was stopped. The heptane was evaporated, and the crude product was purified on a silica gel column, using diethyl ether/*n*-pentane (1:1 by volume) as eluant. The pure product was obtained as orange or ruby red crystals at −70 °C from *n*-pentane solutions, yielding 50% of $Ru_2(CO)_6(DAB)$.

When the complexes were used for further reactions, the heptane solutions were filtered by using finely divided silica. The yield of the complexes in solution was almost quantitative except for DAB = glyoxal bis(isopropylimine). With this ligand $Ru_2(CO)_5$[bis[μ-(1-(isopropylamino)-2-(isopropylimino)ethane)]] was found as a side product and some unreacted $Ru_3(CO)_{12}$ was recovered.

Preparations of $Ru_2(CO)_5$(IAE) {IAE = Bis[μ-(1-(*tert*-butylamino)-2-(*tert*-butylimino)ethane-*N*,*N'*)], Bis[μ-(1-(isopropylamino)-2-methyl-2-(isopropylimino)ethane-*N*,*N'*)]}. $Ru_3(CO)_{12}$ (0.33 mmol) and DAB (1.0 mmol) were refluxed for 8 h in toluene. When the reaction was stopped, the product precipitated as yellow crystals. Complete precipitation was obtained at −70 °C. The product was filtered off, washed twice with 10 mL of *n*-pentane and dried in vacuo. The crude product was recrystallized from hot toluene or from dichloromethane at −70 °C; yield 80% of bright yellow cubic crystals.

Preparation of $Ru_2(CO)_5$(IAE) {IAE = Bis[μ-(1-(isopropylamino)-2-(isopropylimino)ethane-*N*,*N'*)], Bis[μ-(1-(cyclohexylamino)-2-(cyclohexylimino)ethane-*N*,*N'*)]}. $Ru_3(CO)_{12}$ (0.33 mmol) and DAB (1.0 mmol) were refluxed in 50 mL of toluene. The reaction was monitored with infrared spectroscopy and was stopped as soon as the characteristic ν(CO) pattern of the $Ru_2(CO)_2$(IAE) complexes appeared (see Figure 6). The time required for complete conversion was approximately 2.5 h. At room temperature the products precipitated as yellow powders, which were recrystallized from dichloromethane at −70 °C, yielding 80% of yellow-orange crystals.

All $Ru_2(CO)_5$(IAE) complexes crystallized at low temperature, but the products which appeared to be regular shaped crystals in fact were powders. All attempts to obtain single crystals failed.

Preparation of $Ru_2(CO)_4$(IAE) {IAE = Bis[μ-(1-(isopropylamino)-2-(isopropylimino)ethane-*N*,*N'*)], Bis[μ-(1-(cyclohexylamino)-2-(cyclohexylimino)ethane-*N*,*N'*)]}. $Ru_3(CO)_{12}$ (0.33 mmol) and DAB (1.0 mmol) were refluxed for 12 h in toluene. At room temperature the product precipitated as yellow crystals. The crude product was recrystallized from hot toluene, and complete crystallization was obtained at −70 °C, yielding 80% of yellow crystals.

Crystals of the cyclohexyl derivative contained toluene in a 1:1 molar ratio with the complex.

Preparations of $Ru_2(CO)_4(DAB)_2$ [DAB = Glyoxal Bis(isopropylimine), Glyoxal Bis(cyclohexylimine)]. $Ru_3(CO)_{12}$ (0.33 mmol) and DAB (1.0 mmol) were stirred for 12 h at 120 °C in xylene. A solution of $Ru_2(CO)_4$(IAE) was formed, which was refluxed for another 72 h. The reaction was monitored by using IR spectroscopy and was stopped when all bands due to $Ru_2(CO)_4$(IAE) had disappeared. The complexes precipitated as yellow powders at room temperature and were recrystallized from dichloromethane at −70 °C, yielding 80% of yellow crystals.

Crystals of the cyclohexyl derivative contained dichloromethane in a 1:1 molar ratio with the product.

Preparation of $Ru_2(CO)_4(DAB)_2$ [DAB = Glyoxal Bis(*p*-tolylimine)]. $Ru_3(CO)_{12}$ (0.33 mmol) and DAB (1.0 mmol) were refluxed in 50 mL of toluene for 2 h. The crude product precipitated at room temperature, and complete precipitation was obtained at −70 °C. The product was recrystallized from hot toluene, yielding 90% of orange crystals.

Table I. Observed and Calculated Molecular Weights and IR Absorption Data of $Ru_2(CO)_6$(DAB), $Ru_2(CO)_5$(IAE), $Ru_2(CO)_4$(IAE), and $Ru_2(CO)_4(DAB)_2$

	M_r^{a}						
R_1, R_2	calcd	found	ν(CO), cm^{-1}				
		$Ru_2(CO)_6$(DAB)					
t-Bu, H	538.48	539	2069	2030	1994	1983	1961^b
i-Pr, H	510.26	511	2067	2025	1991	1988	1961^b
cHx, H	590.60	591	2067	2024	1996	1984	1960^b
i-Pr, H/CH_3	524.29	525	2065	2025	1993	1981	1956^b
		$Ru_2(CO)_5$(IAE)					
t-Bu, H	678.75	679	2021	1989	1939	1699	^{c}
i-Pr, H	622.65	623	2021	1991	1937	1688	^{c}
cHx, H	782.89	783	2018	1991	1935	1689	^{c}
i-Pr, H/CH_3	650.75	651	2018	1989	1935	1689	^{c}
		$Ru_2(CO)_4$(IAE)					
i-Pr, H	594.64	596	1988	1946	1904	^{c}	
cHx, H	754.88	756	1984	1943	1899	^{c}	
		$Ru_2(CO)_4(DAB)_2$					
i-Pr, H	594.64	596	1983	1922	^{c}		
cHx, H	754.88	756	1974	1905	^{c}		
p-tol, H	786.22	787	1996	1934	^{c}		

[a] The molecular weights have been taken from the mass spectra. The reported values account for the highest peak of the isotope pattern, resulting from Ru_2 fragments with a total mass of 202. The molecular weights of the complexes in solution (VPO measurements in chloroform) are in agreement with the molecular weights obtained by mass spectroscopy. [b] Solvent *n*-pentane. [c] Solvent dichloromethane.

Alternative Reaction Routes. $Ru_2(CO)_5$(IAE), $Ru_2(CO)_4$(IAE) and $Ru_2(CO)_4(DAB)_2$ could all be prepared by starting from the corresponding $Ru_2(CO)_6$(DAB) complexes, by reacting them with an equimolar amount of DAB ligand with use of the same solvent as was described for the direct syntheses starting from $Ru_3(CO)_{12}$. However, all reaction times were approximately 1 h shorter.

Since $Ru_2(CO)_6$[glyoxal bis(*p*-tolylimine)] could not be isolated, the alternative method could not be applied for the preparation of $Ru_2(CO)_4$[glyoxal bis(*p*-tolylimine)]$_2$.

With application of the alternative method, $Ru_2(CO)_5$(IAE) complexes could be obtained containing two inequivalent aliphatic DAB ligand fragments (R = *t*-Bu, *i*-Pr, cHx).

Preparations of $Fe_2(CO)_6$(DAB) [DAB = Glyoxal Bis(*tert*-butylimine), Glyoxal Bis(isopropylimine), Glyoxal Bis(cyclohexylimine), Glyoxal Bis(*p*-tolylimine), Methylglyoxal Bis(isopropylimine)]. $Fe_2(CO)_9$ (3 mmol) and DAB (3 mmol) were refluxed for 48 h in 50 mL of hexane. $Fe(CO)_3$(DAB) and $Fe_2(CO)_6$(DAB) were both found and were difficult to separate. The $Fe(CO)_3$(DAB) complexes were destroyed by stirring of the solution in air for $^1/_2$ h. The hexane was evaporated, and the residue was purified by chromatography on silica gel, using *n*-pentane as eluant. The first fraction containing the product was collected and evaporated down to 50 mL. The crude product precipitated at −70 °C to yield 30% of dark brown crystalline $Fe_2(CO)_6$(DAB).

Analytical Data. Elemental analyses were carried out by the Elemental Analysis Section of the Institute for Organic Chemistry, TNO, Utrecht, The Netherlands, and gave satisfactory results, except for the two $Ru_2(CO)_6$(DAB) complexes containing isopropyl groups. The solid crystalline products rapidly decomposed even in a nitrogen atmosphere. Therefore, these complexes have been characterized by spectroscopy only. The complexes gave characteristic IR absorptions which are listed in Table I. Mass spectra have been recorded by using field desorption technique. The observed and calculated molecular weights are included in Table I.

Crystal Structure Determination of Tetracarbonylbis[glyoxal bis(isopropylimine)]diruthenium. Monoclinic crystals were obtained from a dilute dichloromethane solution at 30 °C.

Cell constants, measured at room temperature with use of a Nonius CAD 4 diffractometer with graphite Cu Kα radiation, are a = 17.274 (1) Å, b = 10.468 (1) Å, c = 14.387 (1) Å, β = 108.864 (4)°, Z = 4, d(calcd) = 1.604 g cm^{-3}, and d(measd) = 1.59 g cm^{-3} (by flotation).

For the data collection a crystal (0.20 × 0.15 × 0.13 mm) mounted along [100] was selected, and out of 2153 measured intensities, 1909

Table II. Positional Parameters Involving All Nonhydrogen Atoms

	x	*y*	*z*
Ru	−0.25806 (2)	0.6777 (5)	0.3978 (3)
C(1)	−0.1824 (4)	0.9562 (6)	0.4709 (5)
C(2)	−0.2482 (4)	0.8821 (6)	0.4045 (4)
C(3)	−0.3925 (4)	0.8730 (7)	0.3909 (5)
C(4)	−0.4554 (5)	0.7902 (8)	0.4156 (6)
C(5)	−0.4042 (5)	1.0156 (8)	0.4101 (6)
C(6)	0.1149 (5)	1.0484 (8)	0.6325 (6)
C(7)	−0.0552 (6)	1.1138 (10)	0.5882 (7)
C(8)	−0.1635 (6)	1.1477 (10)	0.6707 (7)
C(9)	−0.1721 (4)	0.5916 (7)	0.3601 (5)
C(10)	−0.3088 (4)	0.3161 (7)	0.7667 (5)
N(1)	−0.1765 (3)	0.9641 (5)	0.5624 (3)
N(2)	−0.3072 (3)	0.8320 (5)	0.4452 (4)
O(1)	−0.1241 (4)	0.5447 (6)	0.3285 (5)
O(2)	−0.3448 (4)	0.6844 (6)	0.1822 (4)

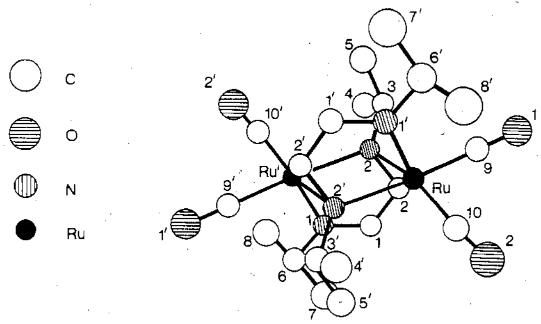

Figure 2. Molecular structure of tetracarbonylbis[glyoxal bis(isopropylimine)]diruthenium with the numbering of the atoms.

were significantly above the background level ($I > 2.5\sigma_I$). From the systematic extinctions it was deduced that the space group was either $C2/c$ or Cc. No absorption correction was applied since the main interest of the investigation was the configuration of the molecule. Moreover, the size of the crystal was small enough so that neglecting the absorption correction did not influence the positional parameters, because in the difference synthesis at the stage $R = 4.6\%$ the residual density near the Ru atoms did not exceed 0.5 e/Å^3.

The ruthenium positions were determined in space group $C2/c$ from a Patterson function and the carbon, nitrogen, and oxygen positions from a subsequent difference Fourier map. The refinement was carried out with a block-diagonal least-squares procedure, using the Cruickshrank weighting scheme and applying anisotropic thermal parameters for the ruthenium atoms and isotropic ones for the carbon, nitrogen, and oxygen atoms. The final R value was 4.6%. In the difference synthesis hydrogen atoms could be located, but they are not used for further refinement. A refinement in the noncentrosymmetric space group Cc was not significantly better than the refinement in $C2/c$ so that the latter space group is the correct one.

The molecular structure of tetracarbonylbis[glyoxal bis(isopropylimine)]diruthenium with the numbering of the atoms is shown in Figure 2, and a stereoview of the molecule is shown in Figure 3. In Table II the atomic parameters are given, in Table III the bond lengths are given, in Table IV the bond angles are given, and in Table V the angles are given between some intramolecular planes, giving a better view on the geometry of the molecule.

Table III. Bond Lengths (Å) Involving All Nonhydrogen Atoms

Ru–Ru′	3.308 (1)	N(2)–C(2)	1.43 (1)
Ru–N(2)	2.14 (1)	N(2)–C(3)	1.49 (1)
Ru′–N(2)	2.11 (1)	C(1)–C(2)	1.45 (1)
Ru′–N(1)	2.16 (1)	C(3)–C(4)	1.52 (1)
Ru–C(2)	2.14 (1)	C(3)–C(5)	1.54 (1)
Ru–C(9)	1.86 (1)	C(6)–C(7)	1.54 (2)
Ru–C(10)	1.83 (1)	C(6)–C(8)	1.54 (2)
N(1)–C(1)	1.30 (1)	C(9)–O(1)	1.17 (1)
N(1)–C(6)	1.49 (1)	C(10)–O(2)	1.17 (1)

Table IV. Bond Angles (Deg) Involving All Nonhydrogen Atoms[a]

N(2)–Ru–N′(2)	78.7 (2)	C(2)–N(2)–C(3)	113.2 (5)
N(2)–Ru–N′(1)	94.2 (2)	C(2)–N(2)–Ru′	107.1 (3)
N(2)–Ru–C(9)	157.9 (3)	C(3)–N(2)–Ru′	127.6 (5)
N(2)–Ru–C(10)	98.7 (3)	Ru–C(2)–N(2)	69.2 (3)
N(2)–Ru–C(2)	39.4 (3)	Ru–C(2)–C(1)	124.4 (5)
N′(1)–Ru–C(10)	97.3 (3)	N(2)–C(2)–C(1)	115.9 (6)
N′(1)–Ru–C(9)	106.8 (3)	C(2)–C(1)–N(1)	119.6 (7)
N′(1)–Ru–C(2)	133.5 (3)	C(1)–N(1)–C(6)	122.1 (7)
N′(1)–Ru–N′(2)	78.6 (2)	C(1)–N(1)–Ru′	111.6 (5)
C(9)–Ru–C(10)	85.6 (3)	C(6)–N(1)–Ru′	125.5 (5)
C(9)–Ru–C(2)	119.5 (3)	N(2)–C(3)–C(4)	111.8 (6)
C(9)–Ru–N′(2)	98.4 (3)	N(2)–C(3)–C(5)	110.5 (6)
C(10)–Ru–N′(2)	174.9 (3)	C(4)–C(3)–C(5)	111.3 (7)
C(10)–Ru–C(2)	90.5 (3)	N(1)–C(6)–C(7)	114.2 (7)
C(2)–Ru–N′(2)	90.2 (2)	N(1)–C(6)–C(8)	106.8 (7)
Ru–N(2)–Ru′	101.3 (2)	C(7)–C(6)–C(8)	111.0 (8)
Ru–N(2)–C(2)	71.4 (4)	Ru–C(9)–O(1)	173.4 (7)
Ru–N(2)–C(3)	122.2 (4)	Ru–C(10)–O(2)	178.0 (7)

[a] Esd's are given in parentheses.

Table V. Angles (Deg) between Some Intramolecular Planes

plane		angle
Ru–N(2)–Ru′–N′(2)	C(9)–Ru–C(10)	22.9
Ru–N(2)–Ru′–N′(2)	Ru–N(1)–Ru′–N′(1)	77.7
Ru–N(2)–Ru′–N′(2)	Ru–N(1)–C(1)	79.7
Ru–N(1)–C(1)	Ru–C(9)–C(10)	78.1

Results and Discussion

Molecular Structure of Tetracarbonylbis[glyoxal bis(isopropylimino)]diruthenium. The asymmetric unit of the unit cell contains half a molecule. The molecule itself is situated around the center of symmetry at 0.75, 0.75, 0.5.

Since the Ru–Ru distance is 3.308 (1) Å, there is no metal–metal bond present. The two halves of the molecule are kept together by the bridging function of the μ^2-N(2),η^2-C(2)N(2) coordinated imine fragments of the two DAB ligands; the Ru–N(2) distance is 2.14 (1) Å, and the Ru′–N(2) distance is 2.11 (1) Å. In the C(2)–N(2) bridge there is a Ru–C(2) bond of 2.14 (1) Å. This clearly demonstrates that the Ru–Ru bond and a carbon–carbon bond of the reactant $Ru_2(CO)_4$(IAE) are broken.

The C(2)–N(2) bond of 1.43 (1) Å is significantly longer than the C(1)–N(1) double bond of 1.30 (1) Å. The bond lengths in the N(1)–C(1)–C(2)–N(2) fragment are comparable with the bond lengths of the N═C—C═N fragment

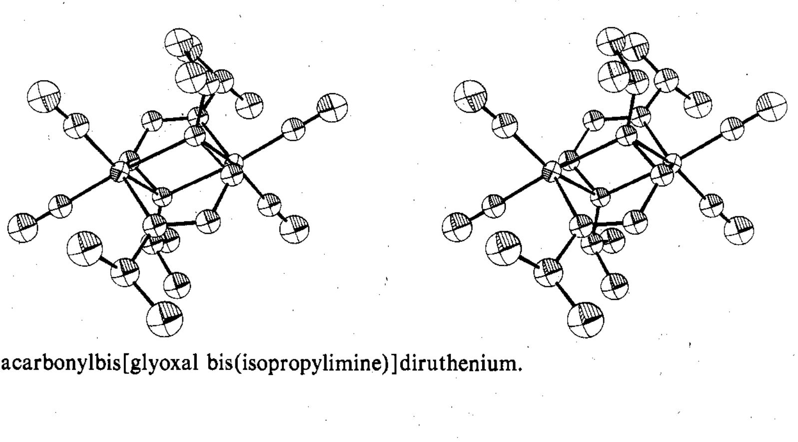

Figure 3. Stereoview of tetracarbonylbis[glyoxal bis(isopropylimine)]diruthenium.

Table VI. ^{1}H NMR Data of $Fe_2(CO)_6(DAB)$, $Ru_2(CO)_6(DAB)$, $Ru_2(CO)_5(IAE)$, $Ru_2(CO)_4(IAE)$, and $Ru_2(CO)_4(DAB)_2$

R_1, R_2 (solvent)[a]	substituents[b]	amine(am)-imine(im) hydrogens ($J = 2$ Hz)	
	$Fe_2(CO)_6(DAB)$		
t-Bu, H (a)	1.20, 1.53 (*t*-Bu)	3.33 (im)	7.36 (im)
i-Pr, H (a)	1.02/1.15, 1.58/1.68 (*i*-Pr)	3.30 (im)	7.52 (im)
i-Pr, H/CH_3 (d)[c]	0.77/0.78, 1.35/1.49 (*i*-Pr), 2.66, 3.26 (*i*-Pr, sept), 1.04 (CH_3)	2.83 (im)	
p-tol, H (a)	2.26, 2.37 (*p*-tol), 7.09, 7.23 (*p*-tol)	3.74 (im)	7.70 (im)
	$Ru_2(CO)_6(DAB)$		
t-Bu, H (a)	1.20, 1.40 (*t*-Bu)	3.41 (im)	7.79 (im)
i-Pr, H (a)	1.02/1.09, 1.37/1.43 (*i*-Pr), 3.18 (*i*-Pr, sept)	3.24 (im)	7.70 (im)
i-Pr, H/CH_3 (a)	1.11/1.21, 1.39/1.51 (*i*-Pr), 1.87 (CH_3), 3.18, 3.49 (*i*-Pr, sept)	3.39 (im)	
cHx, H (a)	1.2, 1.8 (cHx), 2.8 (cHx, br)	3.27 (im)	7.74 (im)
	$Ru_2(CO)_5(IAE)$		
t-Bu, H (a)	1.13, 1.47 (*t*-Bu)	3.87 (am)	8.41 (im)
i-Pr, H (a)	1.04/1.11, 1.26/1.30 (*i*-Pr), 3.3, 3.77 (*i*-Pr, sept)	3.43 (am)	8.08 (im)
i-Pr, H/CH_3 (a)	0.98/1.15, 1.27/1.29 (*i*-Pr), 2.18 (CH_3), 3.2, 3.85 (*i*-Pr, sept)	3.20 (am)	
cHx, H (c)	1–2 (cHx), 2.8 (cHx, br)	3.34 (am)	7.90 (im)
	$Ru_2(CO)_4(IAE)$		
i-Pr, H (b)	1.03/1.07 (*i*-Pr), 1.33 (*i*-Pr), 3.64, 3.68 (*i*-Pr, sept)	3.77 (am)	8.40 (im)
cHx, H (b)	1–2 (cHx), 3.20 (cHx, br)	3.50 (am)	8.12 (im)
	$Ru_2(CO)_4(DAB)_2$		
(*i*-Pr, H)$_2$ (a)	0.80/0.84, 1.28 (*i*-Pr), 1.80, 3.70 (*i*-Pr, sept)	4.08 (im)	8.23, 8.25 (im)[d]
(cHx, H)$_2$ (a)	1–2 (cHx), 3.40 (cHx, br)	4.31 (im)	8.43 (im)
(*p*-tol, H)$_2$ (a)	2.08, 2.21 (*p*-tol), 6.78, 7.01 (*p*-tol)	5.54 (im)	8.83 (im)

[a] Solvent: a, $CDCl_3$; b, acetone; c, CD_2Cl_2; d, C_6D_6. δ is relative to Me_4Si. [b] Two values separated by a vertical bar correspond to the two signals of diastereotopic isopropyl groups. [c] The compound decomposed too fast in chloroform to obtain sharp signals. [d] Two imine signals at 8.23 and 8.25 ppm due to the appearance of a second isomer.

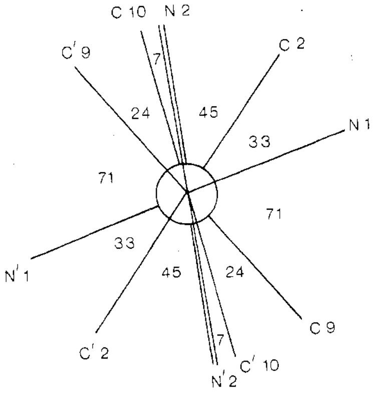

Figure 4. Newman projection along the Ru–Ru′ axis of tetracarbonylbis[glyoxal bis(isopropylimine)]diruthenium.

in $Fe_2(CO)_6(DAB)$,[18] which complexes contain only one DAB ligand coordinated in the "σ,π-coordination" mode.

The angle between C(1)–N(1) and C(2)–N(2) bonds is 5.6°, implying that the planarity of the DAB ligands is not greatly disturbed by the asymmetric coordination.

In the $Ru_2(CO)_4(DAB)_2$ complexes, ruthenium is six-coordinated, and the ligands form a distorted octahedron. The geometry around the ruthenium atoms is shown in the Newman projection along the Ru–Ru′ axis (Figure 4).

^{1}H NMR Data. A remarkable upfield shift of the imine proton resonances can be observed in the $Ru_2(CO)_6(DAB)$, $Ru_2(CO)_n(IAE)$ ($n = 4, 5$), and $Ru_2(CO)_4(DAB)_2$ complexes, compared with the chemical shift values found for complexes containing the DAB ligand in the σ,σ coordination mode.[5,9,10,19] In the free ligands the imine protons give resonances near 7.8 ppm, and in the σ,σ-coordinated complexes values between 7 and 9 ppm have observed (δ relative to Me_4Si).

In $CDCl_3$ solutions the imine protons of $Ru_2(CO)_6(DAB)$ complexes appear as an AX pattern at 7.8 and 3.3 ppm ($J_{AX} = 2.2$ Hz). The μ^2-N,η^2-C=N coordination of one of the imine fragments causes a drastic shielding of the imine proton attached to this fragment. The asymmetric coordination also results in two separate signals for the substituents attached to the nitrogen atoms. The ^{1}H NMR chemical shifts of $Ru_2(CO)_6$[methylglyoxal bis(isopropylimine)] evidence that the N=C(H) fragment is exclusively μ^2-N,η^2-C=N coordinated. The ^{1}H NMR data, including the ^{1}H NMR data of $Fe_2(CO)_6(DAB)$, are listed in Table VI.

Only one earlier example is known of "σ,π-coordinated" DAB, i.e., $Fe_2(CO)_6(DAB)$.[18] Of these complexes only the ^{1}H NMR chemical shifts of the *tert*-butyl derivative have been reported, obtained from a C_6D_6 solution. For a more complete comparison between the $Fe_2(CO)_6(DAB)$ and the $Ru_2(CO)_6(DAB)$ complexes the ^{1}H NMR spectra of an analogous series have been measured in $CDCl_3$ solutions. The results are listed in Table VI. There is no significant difference between the chemical shift values for $Fe_2(CO)_6(DAB)$ and $Ru_2(CO)_6(DAB)$, which strongly indicates that these complexes are isostructural.

The ^{1}H NMR patterns of $Ru_2(CO)_5(IAE)$ and $Ru_2(CO)_4(IAE)$ complexes are comparable to those of the corresponding $Ru_2(CO)_6(DAB)$ complexes. Both imine protons are equivalent and appear as a doublet at 8.2 ppm, while the two equivalent protons on the amine positions (the 1 positions in the IAE ligand) give a doublet at 3.8 ppm ($J_{AX} = 2.0$ Hz). The chemical shifts of the IAE complexes are slightly downfield compared with the values obtained for $M_2(CO)_6(DAB)$ (M = Fe, Ru). The ^{1}H NMR spectra of $Ru_2(CO)_5(IAE)$ and $Ru_2(CO)_4(IAE)$ are almost identical with the spectra of $Mo_2(CO)_6(IAE)$,[17] which is in agreement with the proposed structures.

The ^{1}H NMR spectra of $Ru_2(CO)_4(DAB)_2$ complexes with aliphatic substituents attached to nitrogen are remarkably different from the ^{1}H NMR spectra of $Ru_2(CO)_6(DAB)$ and $Ru_2(CO)_n(IAE)$ ($n = 4, 5$), especially in the case of the isopropyl derivatives. The isopropyl group attached to the μ^2-N,η^2-C=N-coordinated imine moiety is highly shielded. The septet appears at 1.80 ppm and the doublet of the methyls at

---

(18) H. W. Frühauf, A. Landers, R. Goddard, and C. Krüger, *Angew. Chem.*, **90**, 56 (1978).
(19) H. tom Dieck, I. W. Renk, and K. D. Franz, *J. Organomet. Chem.*, **94**, 417 (1975).

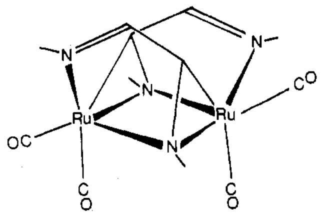

Figure 5. The second isomer of tetracarbonylbis[glyoxal bis(isopropylimine)]diruthenium.

0.8 ppm. The corresponding signals of the isopropyl group attached to the σ-coordinated imine moiety are found at 3.70 and 1.28 ppm.

The ^{1}H NMR spectrum of $Ru_2(CO)_4$[glyoxal bis(isopropylimine)]$_2$ is slightly more complicated than the ^{1}H NMR spectra of other $Ru_2(CO)_4(DAB)_2$ complexes. The imine protons attached to the μ^2-N,η^2-C=N-coordinated imine fragments give one doublet at 4.08 ppm, as was anticipated, but the imine protons attached to the σ-coordinated imine fragments unexpectedly give two doublets at 8.25 and 8.23 ppm, in almost equal intensity. However, the crystal structure of the complex shows a centrosymmetric molecule, and consequently both imine protons are equal and should give only one doublet at 8.2 ppm. After several molecular models were studied, it was obvious that $Ru_2(CO)_4$[glyoxal bis(isopropylimine)]$_2$ can exist in principle in two isomeric forms which give almost identical NMR spectra. The first isomeric form is shown in the molecule structure in Figure 2. The second isomer is shown in Figure 5. The difference between the two isomers is that in the first form one DAB is located below the Ru–N(2)–Ru′–N(2)′ plane and the other DAB ligand above, while in the second form both DAB ligands are on one side of the molecule and the carbonyl groups on the other side.

Exchange experiments in 1,1,2,2-tetrachlorodideuterioethane at 120 °C gave negative results. No exchange between the two isomeric forms could be observed.

For other derivatives of $Ru_2(CO)_4(DAB)_2$ (R = *p*-tolyl or cyclohexyl), no evidence could be found for the existence of two isomers. Whether only one isomer is formed or whether the spectroscopic properties of the two possible isomeric forms are equal is a question that cannot be answered at this time.

The imine protons of $Ru_2(CO)_4$[glyoxal bis(*p*-tolylimine)]$_2$ appear at 8.83 and 5.54 ppm (J_{AX} = 2 Hz) which is at remarkably lower field than in the corresponding complexes with aliphatic ligands. The chemical shifts of the imine protons in $Ru_2(CO)_4$[glyoxal bis(*p*-tolylimine)]$_2$ are in the same region as observed for $MnCo(CO)_6(DAB)$ and $ReCo(CO)_6(DAB)$.[16] The imine proton shifts are also downfield compared with $Fe_2(CO)_6$[glyoxal bis(*p*-tolylimine)] (see Table VI). Consequently, the deshielding effect is not caused by the *p*-tolyl group but is the result of a different interaction between the aromatic DAB ligands and the $Ru_2(CO)_4$ fragment, compared with the situation in complexes containing aliphatic substituted DAB ligands. This will be discussed in more detail in a next section.

For the complexes mentioned in Table VI, the ones with isopropyl groups attached to the skeleton give a diastereotopic splitting of the ^{1}H NMR signals of the isopropyl methyl groups. The splitting in $Ru_2(CO)_n(IAE)$ (n = 4, 5) is identical with the splitting observed for $Mo_2(CO)_6(IAE)$ (R = *i*-Pr).[17]

IR Data (Carbonyl Stretching Region). All complexes have a characteristic ν(CO) absorption spectrum. $Ru_2(CO)_6(DAB)$ complexes have five very intense IR absorption bands between 1900 and 2100 cm^{-1}, which are shown for $Ru_2(CO)_6$[glyoxal bis(cyclohexylimine)] in Figure 6a. The absorption pattern of $Ru_2(CO)_6(DAB)$ complexes is similar to that of $Fe_2(CO)_6(DAB)$.[18] The absorption maxima for all ruthenium complexes are listed in Table I.

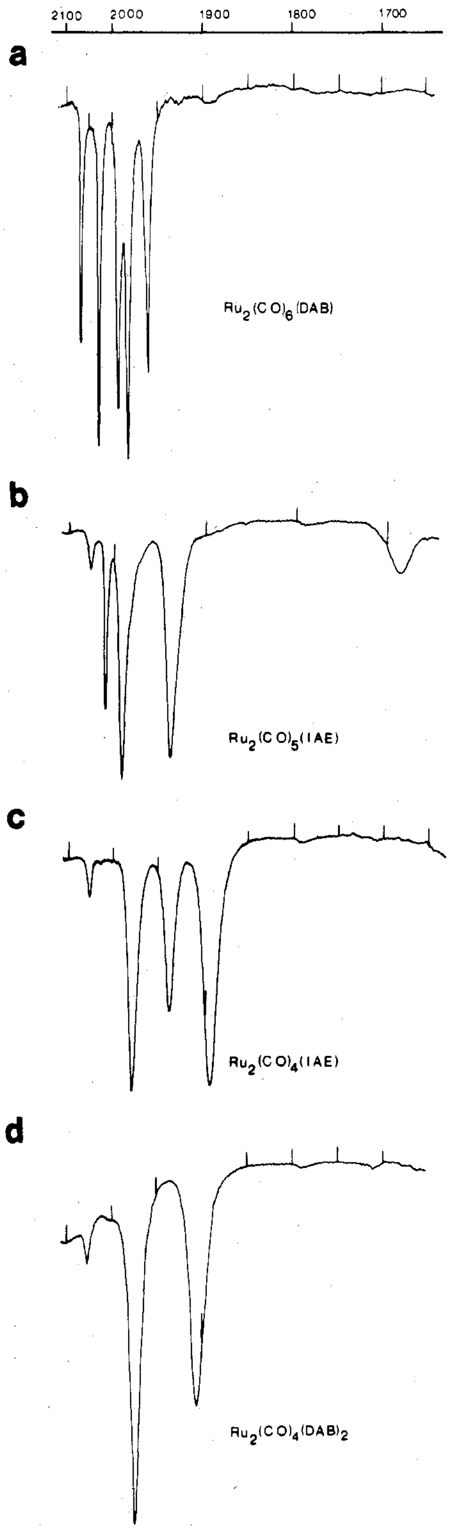

Figure 6. The ν(CO) absorption patterns of $Ru_2(CO)_6(DAB)$, $Ru_2(CO)_5(IAE)$, $Ru_2(CO)_4(IAE)$, and $Ru_2(CO)_4(DAB)_2$ (R = cHx).

$Ru_2(CO)_5(IAE)$ complexes have three absorption bands between 2100 and 1900 cm^{-1}, originating from terminal carbonyl groups and one vibration near 1700 cm^{-1} originating from a bridging carbonyl group. The IR absorption spectrum of the cyclohexyl derivative is shown in Figure 6b. The absorption pattern of $Ru_2(CO)_5(IAE)$ is similar to the pattern which was observed for $Fe_2(CO)_5(C_8H_8)$.[20] The latter com-

---

(20) F. A. Cotton, L. Kruczynski, and B. A. Franz, *J. Organomet. Chem.*, **160**, 93 (1978).

plexes also contain four terminal and one bridging carbonyl group. The absorption of the bridging carbonyl in the iron complex was observed at 1800 cm^{-1}. The energy difference with the bridging carbonyl in $Ru_2(CO)_5(IAE)$ is caused by the presence of a metal–metal bond in $Fe_2(CO)_5(C_8H_8)$, while no metal–metal bond is present in $Ru_2(CO)_5(IAE)$ (vide infra). The bridging carbonyl in $Ru_2(CO)_5(IAE)$ is behaving like a metalloketone.[21] In the CO stretching region of the IR spectra of $Ru_2(CO)_4(IAE)$ complexes, the frequency of the bridging carbonyl disappeared, and three absorption bands were observed between 2000 and 1850 cm^{-1}, originating from four terminal carbonyl groups. The spectrum of the cyclohexyl derivative is shown in Figure 6c.

The IR spectra of $Ru_2(CO)_4(DAB)_2$ complexes consist of only two intense peaks between 2000 and 1900 cm^{-1}, as shown in Figure 6d for $Ru_2(CO)_4$[glyoxal bis(cyclohexylimine)]$_2$. Because of the high symmetry in the molecules, the four CO groups give only two intensities.

The two isomers which were deduced for $Ru_2(CO)_4$[glyoxal bis(isopropylimine)]$_2$ on the basis of the ^{1}H NMR spectra could not be distinguished in the IR absorption spectra.

The differences in the IR spectra of the ruthenium complexes make it possible to monitor the reactions between $Ru_3(CO)_{12}$ and DAB ligands and to stop the reaction as soon as the desired product is formed. Especially when one wished to obtain $Ru_2(CO)_5(IAE)$ (R = cyclohexyl, isopropyl), the reaction should be followed carefully and stopped when the ν(CO) pattern shown in Figure 6b appears.

UV–Visible Measurements. In the UV spectra of binuclear metal carbonyl complexes containing a two-electron metal–metal bond, an intense ($\epsilon \approx 15000$) ligand field transition (LF) can be observed which is generally assigned to the $\sigma \rightarrow \sigma^*$ transition localized on the metal–metal bond.[10,17,22-31] The intensity of this transition increases at lower temperature. Although the origin of this intensity increase is still unknown, the effect can be used as a tool to determine whether a metal–metal bond is present in the complexes.[32]

The low-temperature UV–visible spectra of $Ru_3(CO)_{12}$ have been investigated to check whether the effect also appears in ruthenium carbonyl complexes. A large low-temperature increase of the intensity of the $\sigma \rightarrow \sigma^*$ transition was observed. This is the first example of the low-temperature behavior in a metal carbonyl cluster.

The UV–visible spectra of $Ru_2(CO)_6(DAB)$ and $Ru_2(CO)_4(DAB)_2$ show broad unstructured bands below 400 nm from which no reliable information can be obtained. More information can be obtained from the UV–visible spectra of $Ru_2(CO)_5(IAE)$ and $Ru_2(CO)_4(IAE)$. For $Ru_2(CO)_4(IAE)$ an intense band at 290 nm is observed, which increases at lower temperature. This band is assigned to the $\sigma \rightarrow \sigma^*$ transition localized on the Ru–Ru bond (see also Figure 7b). In Figure 7a the UV spectra of $Ru_2(CO)_5(IAE)$ (R = *t*-Bu) are shown, for which this phenomenon is not observed. The band at 290 nm is absent, which is in agreement with the proposed structure for $Ru_2(CO)_5(IAE)$.

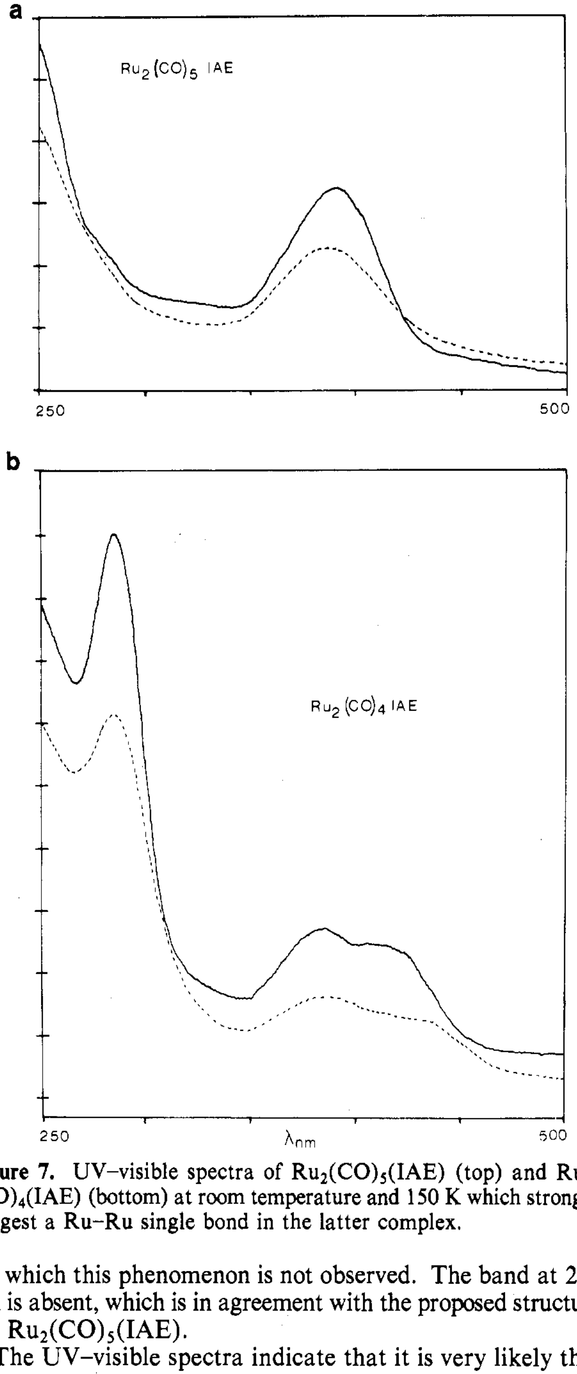

Figure 7. UV–visible spectra of $Ru_2(CO)_5(IAE)$ (top) and $Ru_2(CO)_4(IAE)$ (bottom) at room temperature and 150 K which strongly suggest a Ru–Ru single bond in the latter complex.

The UV–visible spectra indicate that it is very likely that there is a two-electron metal–metal bond present in $Ru_2(CO)_4(IAE)$ complexes, while such a bond is absent in the case of $Ru_2(CO)_5(IAE)$.

Mass Spectrometry. The mass spectra have been recorded for all the complexes listed in Table I. The parent-ion peaks of all complexes have been observed, and the peaks related to the ^{101}Ru isotopes are in agreement with the calculated molecular weights (see Table I). The molecular weights determined in solution (VPO measurements in chloroform) also suggested a binuclear structure for all complexes.

The mass spectra of the binuclear ruthenium complexes have a characteristic isotope pattern. The calculated and observed mass spectra are in good agreement. The pattern with the highest intensity is of a $[Ru_2(CO)_5(DAB)]^+$ fragment. Further fragmentation than the loss of one carbonyl group was not observed, since FD technique was applied.

Formation of the Complexes. All preparations must be carried out in a nitrogen atmosphere since in all reactions a highly air-sensitive red solution was formed in the first step,

---

(21) M. P. Brown, A. N. Keith, Lj. Manojlović-Muir, K. W. Muir, R. J. Puddephatt, and S. R. Seddon *Inorg. Chim. Acta*, **34**, L223 (1979).

(22) J. L. Hughey, C. P. Anderson, and Th. J. Meijer, *J. Organomet. Chem.*, **125**, C49 (1977).

(23) S. A. Hallock and A. Wojcicki, *J. Organomet. Chem.*, **54**, C527 (1973).

(24) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 2065 (1975).

(25) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 4246 (1975).

(26) D. S. Ginley and M. S. Wrighton, *J. Am. Chem. Soc.*, **97**, 4908 (1975).

(27) R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 6042 (1975).

(28) D. L. Morse and M. S. Wrighton, *J. Am. Chem. Soc.*, **98**, 3931 (1976).

(29) R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Am. Chem. Soc.*, **92**, 3654 (1970).

(30) D. S. Ginley, C. R. Bock, and M. S. Wrighton, *Inorg. Chim. Acta*, **23**, 85 (1977).

(31) H. B. Abrahamson, C. C. Frazier, D. S. Ginley, H. B. Gray, J. J. Lilienthal, D. R. Thyler, and M. S. Wrighton, *Inorg. Chem.*, **16**, 1554 (1977).

(32) The occurrence of the low-temperature increase can be used as evidence for the presence of a metal–metal bond. However, when the effect is not observed, there is still the possibility of a metal–metal bond.

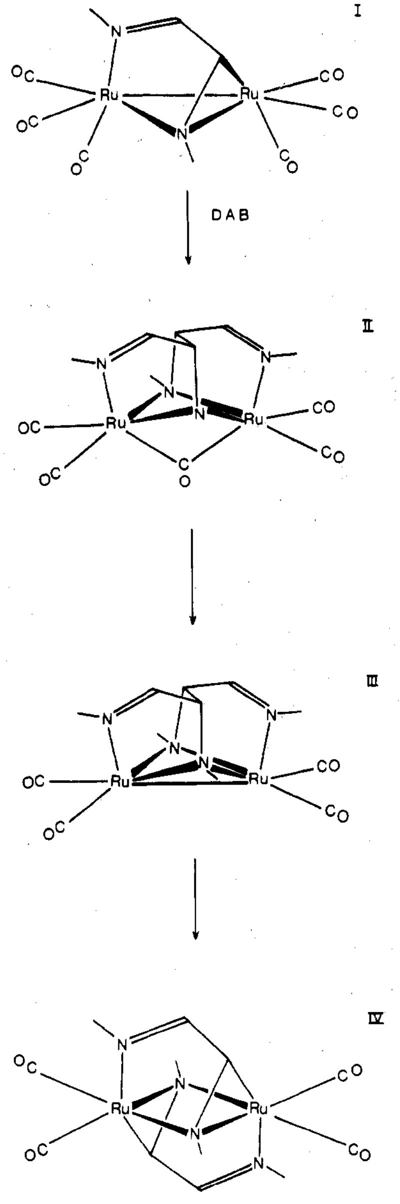

Figure 8. Reaction sequence of the reaction between $Ru_3(CO)_{12}$ and DAB showing the isolated products: I, $Ru_2(CO)_6(DAB)$; II, $Ru_2(CO)_5(IAE)$; III, $Ru_2(CO)_4(IAE)$; IV, $Ru_2(CO)_4(DAB)_2$.

of which the nature is still unknown. After a short period the red solution was converted into a solution containing the more stable binuclear complexes.

When $Ru_3(CO)_{12}$ was reacted in a 2:3 molar ratio with DAB ligands, binuclear ruthenium carbonyl complexes were formed containing one DAB ligand coordinated in the "σ,π coordination" mode, according to eq 1. The proposed structure of $Ru_2(CO)_6(DAB)$ is shown in Figure 8(I). The $Ru_2(CO)_6(DAB)$ complexes are isostructural to $Fe_2(CO)_6(DAB)$, for which a crystal structure is known.[18] The binuclear $Ru_2(CO)_6(DAB)$ complexes are formed from the trinuclear $Ru_3(CO)_{12}$ cluster, which means that cluster breakdown must occur.[33]

$$Ru_3(CO)_{12} + {}^3/_2DAB \rightarrow {}^3/_2Ru_2(CO)_6(DAB) + 3CO \quad (1)$$

$Ru_2(CO)_5(IAE)$ can be prepared either from $Ru_3(CO)_{12}$ and DAB or from $Ru_2(CO)_6(DAB)$ and DAB. The reactions are given in eq 2 and 3.

$$Ru_3(CO)_{12} + 3DAB \xrightarrow{\Delta T} {}^3/_2Ru_2(CO)_5(IAE) + {}^9/_2CO \quad (2)$$

$$Ru_2(CO)_6(DAB) + DAB \xrightarrow{\Delta T} Ru_2(CO)_5(IAE) + CO \quad (3)$$

The structure of $Ru_2(CO)_5(IAE)$ is shown in Figure 8(II) and has been proposed on the bases of ^1H NMR data, IR data, and UV-vis spectroscopy. The complexes are analogous to $Mo_2(CO)_6(IAE)$.[17] The fact that $Ru_2(CO)_5(IAE)$ can also be formed from the reaction between $Ru_2(CO)_6(DAB)$ and DAB ligands shows that $Ru_2(CO)_6(DAB)$ can be considered as an intermediate in the reaction sequence. This aspect will be discussed in more detail separately.

$Ru_2(CO)_5(IAE)$ complexes derived from two different DAB ligands can be prepared according to eq 3. However, the mass spectra of these asymmetric IAE complexes show that besides the asymmetric products small amounts (10–20%) of the symmetric $Ru_2(CO)_5(IAE)$ complexes are formed also, which must result from rearrangement reactions.

$Ru_2(CO)_4(IAE)$ can be prepared either from $Ru_3(CO)_{12}$ and DAB according to eq 4 or by an intramolecular reaction of $Ru_2(CO)_5(IAE)$ (eq 5).

$$Ru_3(CO)_{12} + 3DAB \xrightarrow{\Delta T} {}^3/_2Ru_2(CO)_4(IAE) + 6CO \quad (4)$$

$$Ru_2(CO)_5(IAE) \xrightarrow{\Delta T} Ru_2(CO)_4(IAE) + CO \quad (5)$$

The structure of $Ru_2(CO)_4(IAE)$ is shown in Figure 8(III). The main difference between this structure and the structure of $Ru_2(CO)_5(IAE)$ (Figure 8(II)) is that the bridging carbonyl is lost and that a metal–metal bond is formed.

Since $Ru_2(CO)_4(IAE)$ can be prepared from $Ru_2(CO)_5(IAE)$, the latter can be regarded as an intermediate in the formation of $Ru_2(CO)_4(IAE)$ from $Ru_3(CO)_{12}$ and DAB ligands.

After prolonged heating of $Ru_3(CO)_{12}$ and DAB ligands in xylene, $Ru_2(CO)_4(DAB)_2$ complexes are formed according to eq 6. These products can also be obtained starting from $Ru_2(CO)_4(IAE)$ by an intramolecular rearrangement (eq 7). The structure is shown in Figure 2 and as a part of the reaction sequence in Figure 8.

$$Ru_3(CO)_{12} + 3DAB \xrightarrow{\Delta T} {}^3/_2Ru_2(CO)_4(DAB)_2 + 6CO \quad (6)$$

$$Ru_2(CO)_4(IAE) \xrightarrow{\Delta T} Ru_2(CO)_4(DAB)_2 \quad (7)$$

The aromatic DAB ligand glyoxal bis(*p*-tolylimine) is much more reactive than the aliphatic DAB ligands. None of the intermediates isolated for the aliphatic DAB's could be isolated for the aromatic ligand. Only $Ru_2(CO)_5(IAE)$ was found as an unstable intermediate in solution.

In Figure 8 all the products which could be isolated from the reactions between $Ru_3(CO)_{12}$ and DAB ligands are shown. These products could not be isolated for all ligands. As well as the high reactivity of glyoxal bis(*p*-tolylimine) mentioned above, there is also some differentiation in reactivity among the aliphatic diimines. For glyoxal bis(*tert*-butylimine) and for methylglyoxal bis(isopropylimine) the reaction is terminated at the formation of $Ru_2(CO)_5(IAE)$. After reaction times of more than 4 days in refluxing xylene solutions, only traces of $Ru_2(CO)_4(IAE)$ could be detected for the *t*-Bu derivative, while complete decomposition occurred for the methylglyoxal bis(isopropylimine) derivative. Only in the cases of glyoxal bis(isopropylimine) and glyoxal bis(cyclohexylimine) could all the products shown in Figure 8 be isolated and characterized.

---

(33) Analogous to the formation of $Ru_2(CO)_6(DAB)$ from $Ru_3(CO)_{12}$ and DAB, $Os_2(CO)_6(DAB)$ can be formed from $Os_3(CO)_{12}$ and DAB. Mass spectra of the products showed that $Os_3(CO)_9(DAB)$ was formed also. Probably cluster breakdown occurs starting from $M_3(CO)_9(DAB)$ (M = Ru, Os): L. H. Staal, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, in press.

Reaction Mechanism. The reaction sequence in Figure 8 already gives a good indication of how the various binuclear ruthenium carbonyl complexes are formed. However, the formation of IAE ligands from "σ,π-coordinated" DAB ligands is not an obvious step. A few alternatives should be considered.

The fact that the $Ru_2(CO)_4(DAB)_2$ complexes are formed after prolonged heating of $Ru_2(CO)_4(IAE)$ evidences that these complexes with two "σ,π-coordination" DAB ligands can be excluded as intermediates in the formation of IAE systems. Activation of one DAB ligand in $Ru_2(CO)_6(DAB)$ seems sufficient for C–C bond formation. There still remain two alternative reaction pathways: (i) initial coordination of a free DAB ligand to $Ru_2(CO)_6(DAB)$ followed by insertion of a (H)C=N fragment in the Ru–C bond of the η^2-C=N-coordinated imine moiety or (ii) initial insertion followed by coordination of the free imine fragment to the ruthenium carbonyl unit. The first alternative seems less likely, since the geometry of the coordination sites of Ru would force a second DAB ligand into a noninteractive position relative to the "σ,π-coordinated" DAB ligand. This model is in agreement with the insertion reactions of small unsaturated molecules in $Ru_2(CO)_6(DAB)$.[34]

When methylglyoxal bis(isopropylimine) was used as DAB ligand in the formation of $Ru_2(CO)_6(DAB)$, a complex with the methyl group located on the σ-coordinated C=N moiety always resulted. The effect of substituents at the imine carbon atoms on the π-coordinating ability of the C=N fragments causes a regioselective insertion of the DAB ligands, leading to stereospecific syntheses of IAE ligands. Of the three possible isomeric forms of IAE ligands derived from methylglyoxal bis(isopropylimine)[17] (see also Figure 1) the isomer with both methyl groups on the imine positions was formed exclusively. This is in agreement with the proposed reaction pathway for the formation of IAE ligands. In $Ru_2(CO)_6$-[methylglyoxal bis(isopropylimine)] the methyl group is already present on the nonactivated site, and insertion of a (H)C=N moiety will be favored above insertion of a (CH_3)C=N moiety because of the repulsive interaction of the methyl group. The inserting behavior of the (H)C=N moiety is analogous to the behavior of acetylenes. In the insertion reactions of acetylenes at least one hydrogen atom is required on the C≡C fragment.[34]

The methylglyoxal bis(isopropylimine) derivative of $Mo_2(CO)_6(IAE)$ was also formed exclusively in the isomeric form with the two methyl groups on the imine positions.[17] This already suggested a mechanism which involved σ,π coordination. The analogy with the ruthenium carbonyl complexes is in agreement with the basic principle in the proposed mechanism for the formation of $Mo_2(CO)_6(IAE)$. For these complexes σ,π coordination was assumed to be the activating step.[17]

In $Ru_2(CO)_5(IAE)$ and $Ru_2(CO)_4(IAE)$ complexes a carbon–carbon bond is formed between two DAB ligands. A striking feature in the reaction sequence is that this bond can be broken again to form $Ru_2(CO)_4(DAB)_4$ complexes. This behavior is analogous to the cleavage of the IAE ligand in $Mo_2(CO)_6(IAE)$ at elevated temperatures. When $Mo_2(CO)_6(IAE)$ (R = *t*-Bu) was refluxed in xylene for 2 h, the mononuclear $Mo(CO)_4(DAB)$ re-formed together with some decomposition material. Thus in this reaction the selective C–C bond cleavage in the IAE ligand again leads to the formation of two DAB ligands.

When $Fe_2(CO)_6(DAB)$ was reacted with DAB ligands in the same way as was described for $Ru_2(CO)_6(DAB)$, $Fe(CO)_3(DAB)$ complexes were formed. No evidence could be found for the existence of analogous diiron carbonyl IAE complexes.

Obviously, the IAE ligands can be formed in metal carbonyl complexes under suitable reaction conditions, but the reactions discussed above show that the corresponding DAB ligands are thermodynamically more stable. This is in agreement with the fact that at present attempts to isolate the free IAE ligand resulted in the isolation of free DAB ligands. In this respect the relative long C–C bond of 1.61 Å between the two DAB fragments in $Mo_2(CO)_6(IAE)$ might be meaningful,[17] since such a long C–C bond might also be expected for $Ru_2(CO)_n(IAE)$ (n = 4, 5). The relatively long C–C bond distance may be caused by repulsive interaction due to steric crowding around the seven-coordinated molybdenum centers. In the case of $Ru_2(CO)_4(IAE)$ the molecule is strained probably because of the presence of a bent metal–metal bond.

Concluding Remarks

The reaction sequence in Figure 8 can be considered as a model of organic syntheses on a metal surface. Unfortunately so far attempts to separate the organic part from the metal carbonyl nucleus without disrupting the newly formed IAE system have failed. The activating step in the reaction is η^2-C=N coordination of an imine moiety with subsequent insertion of an unsaturated organic molecule in the metal–carbon bond between ruthenium and DAB. In this respect the IAE formation is a special case of C–C bond formation in activated complexes.[34]

IAE formation is analogous to the dimerization of ethyl *N*-(α-methylbenzyl)iminoacetate,[35] on a $Fe_2(CO)_6$ unit. In these complexes a C—C bond is formed between two fragments of N=C—C=O skeletons.

It is possible formally to distinguish between two types of "σ,π coordination". In $M_2(CO)_6(DAB)$ (M = Fe, Ru) the DAB ligands donate six electrons which are equally shared between the two metal centers (3e–3e sharing). In $MCo(CO)_6(DAB)$ (M = Mn, Re) the DAB ligands formally donate four electrons to manganese or rhenium and two electrons to cobalt (4e–2e sharing). For $Ru_2(CO)_4(DAB)_2$ complexes it is not possible to make this formal distinction following the naive approach of electron counting. The NMR spectra of aliphatic DAB complexes (R = isopropyl, cyclohexyl) resemble the spectra of $Ru_2(CO)_6(DAB)$ complexes, containing the DAB ligand in the 3e–3e type of bonding, while the spectra of $Ru_2(CO)_4$[glyoxal bis(*p*-tolylimine)]$_2$ are more in agreement with the spectra of $MCo(CO)_6(DAB)$ (M = Mn, Re), containing the DAB ligand in the 4e–2e bonding type. The delicate balance of electronic distribution seems highly dependent on the subsituents attached to the DAB ligands.

The effect of the substituents on the reactivity and the stability of the complexes was evident from the discussion of the reaction sequence shown in Figure 8 and has been observed before in the formation of $M(CO)_3X(DAB)$ (M = Mn, Re; X = Cl, Br, I).[9] In these complexes the DAB ligands carrying aromatic substituents were less reactive than the aliphatic DAB ligands. Also in the formation of $Mo_2(CO)_6(IAE)$ the difference between aromatic and aliphatic substituted DAB ligands was remarkable. In these latter complexes only aliphatic DAB ligands gave IAE complexes and aromatic DAB ligands seemed unreactive.[17] This is in agreement with the very rapid formation of $Ru_2(CO)_4$[glyoxal bis(*p*-tolylimine)]$_2$ and the formation of monomeric $Mo(CO)_4(DAB)$ as the only product in the attempted synthesis of the $Mo_2(CO)_6(IAE)$

---

(34) Recent results give a better understanding of the role of π coordination in the activation of coordinated C=N fragments. Unsaturated organic molecules containing C≡C, C=C, C=N moieties can easily be inserted in the metal-carbon bond of the "σ,π-coordinated" DAB ligand in $Ru_2(CO)_6(DAB)$. We assume that IAE formation is analogous to the insertion of these small unsaturated organic molecules: L. H. Staal, L. H. Polm, K. Vrieze, F. Ploegen, and C. H. Stam, submitted for publication in *Inorg. Chem.*

(35) A. De Cian and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 249 (1976).

Inorg. Chem. **1980**, *19*, 3351–3356

complex. In the case of the attempted synthesis of the *p*-tolyl derivative of $Mo_2(CO)_6(IAE)$, it appears $Mo_2(CO)_6(IAE)$ is formed but rapidly reconverts back into $Mo(CO)_4(DAB)$. Thus $Mo(CO)_4(DAB)$ would appear unreactive.

A striking feature of IAE formation is that at present good yields are only obtained for second-row transition metals. However, complexes with "σ,π-coordinated" DAB ligands, which is a prerequisite for IAE formation, are also known for first- and third-row transition metals. In these complexes IAE formation has as yet not been observed, although the analogous dimerization of ethyl *N*-(α-methylbenzyl)iminoacetate did occur on a $Fe_2(CO)_6$ fragment.[35] Whether IAE formation is restricted to second-row transition metals, or that under suitable conditions the first- and third-row elements also form IAE complexes, is a subject of further investigation.

Acknowledgment. We wish to thank Mr R. W. Fokkens and Dr. J. v. d. Greef for recording the mass spectra, Mr Heijdenrijk for collecting the crystallographic data, and Dr. J. D. Schagen, Dr. N. v. d. Putten, and Dr. G. J. Olthof for stimulating discussions during the interpretation of the crystallographic data. Dr. H. Schenk is also acknowledged for criticizing the crystallographic section of the manuscript.

Registry No. $Ru_2(CO)_6$(*t*-Bu, H), 74552-68-4; $Ru_2(CO)_6$(*i*-Pr, H), 74552-69-5; $Ru_2(CO)_6$(cHx, H), 74552-70-8; $Ru_2(CO)_6$(*i*-Pr, H/CH_3), 74552-71-9; $Ru_2(CO)_5$(*t*-Bu, H), 72918-61-7; $Ru_2(CO)_5$(*i*-Pr, H), 72918-60-6; $Ru_2(CO)_5$(cHx, H), 74562-46-2; $Ru_2(CO)_5$(*i*-Pr, H/CH_3), 74562-47-3; $Ru_2(CO)_4$(*i*-Pr, H), 72918-62-8; $Ru_2(CO)_4$(cHx, H), 74562-48-4; $Ru_2(CO)_4$(*i*-Pr, H)$_2$, 74552-72-0; $Ru_2(CO)_4$(cHx, H)$_2$, 74562-49-5; $Ru_2(CO)_4$(*p*-tol, H)$_2$, 74552-73-1; $Fe_2(CO)_6$(*t*-Bu, H), 65045-67-2; $Fe_2(CO)_6$(*i*-Pr, H), 74552-74-2; $Fe_2(CO)_6$(*i*-Pr, H/CH_3), 74552-75-3; $Fe_2(CO)_6$(*p*-tol, H), 74552-76-4; $Ru_3(CO)_{12}$, 15243-33-1; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Tables of thermal parameters, elemental analyses, and structure factors and the observed and simulated mass spectra of $Ru_2(CO)_6$[glyoxal bis(cyclohexylimine)] (16 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Bateman Science Center, Arizona State University, Tempe, Arizona 85281

Synthesis, Characterization, and Molecular Structure of Tetraethylammonium Pentakis(isothiocyanato)bis(2,2′-bipyridine)uranate(IV)

R. O. WILEY, R. B. VON DREELE,* and T. M. BROWN*

Received March 18, 1980

The synthesis of tetraethylammonium pentakis(isothiocyanato)bis(2,2′-bipyridine)uranate(IV) has been accomplished, and it was characterized by classical physical methods. The crystal and molecular structure was determined from single-crystal X-ray data collected by the θ–2θ technique on an automated diffractometer. The compound consists of pentakis(isothiocyanato)bis (2,2′-bipyridine)uranate(IV) anions and disordered tetraethylammonium cations. Uranium is bound to nine nitrogen atoms in a highly distorted monocapped square antiprism in which one bipyridine occupies a position bridging the cap and the near square while the other bipyridine spans the opposite edge of the far square. Distortion from the ideal geometry is caused by the small ligand bite of the bipyridine ligand. An alternative description of the coordination geometry is derived from the seven-coordinate pentagonal bipyramid in which each bipyridine ligand is assumed to occupy an axial position with the five thiocyanato ligands forming the pentagonal girdle. The U–N bond distances vary from 2.35 to 2.47 Å for the thiocyanato ligands and from 2.61 to 2.65 Å for the bipyridine ligands. The structure was solved by standard heavy-atom techniques and refined by large-block matrix least squares to a final *R* value of 0.083 for 3878 indpendent observed reflections. The compound crystallized in the monoclinic space group $P2_1/c$, $Z = 4$, with lattice parameters $a = 14.427$ (10) Å, $b = 18.612$ (17) Å, $c = 15.710$ (10) Å, and $\beta = 105.17$ (7)°, $\rho_{obsd} = 1.57$ g cm^{-3} ($\rho_{calcd} = 1.58$ g cm^{-3}).

Introduction

Coordination numbers greater than 8, with the exception of that for $[ReH_9]^{2-}$,[1] are largely limited to the lanthanides and actinides. This is due to the greater metal size required for more than eight ligands. There are a number of examples of metals exhibiting coordination number 9; the majority of these compounds are polymeric rather than monomeric. The title compound $[Et_4N]^+[U(NCS)_5(bpy)_2]^-$, is one of a small number of nine-coordinate uranium compounds,[2,3] and this compound is unique in that it is the first monomeric nine-coordinate compound characterized to be of the type $M(AA)_2L_5$ (AA = bidentate ligand, L = monodentate ligand). Some other examples of compounds displaying nine-coordination are $[M(OH_2)_9]^{3+}$ (M = Pr, Yb,[4] and Ho[5]), $Er(OAc)_3 \cdot 4H_2O$,[6] $Th(trop)_4(OH_2)$,[7] and $CeCl_3 \cdot 7H_2O$.[8]

The coordination polyhedra of nine-coordinate structures are invariably described in terms of either a monocapped square antiprism (MSAP) or a tricapped trigonal prism (TTP). "Points on a sphere" repulsive calculations[9] show the TTP to be the most favored coordination geometry. However, the difference in energy between the TTP and the MSAP is less than 0.1% of the total energy of either form. Various means of assigning the correct coordination polyhedron to a nine-coordinate structure have been proposed.[9–12] Identification is achieved either by examination of the dihedral angles formed by triangular faces or by comparison to the ideal polyhedron by means of a least-squares-fit calculation.[11] In the instance of a structure strongly distorted by multidentate ligands, this second method is the best since the dihedral angles will vary wildly, and unpredictably, from the ideal values for either the

---

(1) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 555 (1964).
(2) H. Sakurai, C. Miyake, and S. Imoto, *J. Inorg. Nucl. Chem.*, **41**, 1065 (1979).
(3) L. Baracco, G. Bombieri, S. Degetto, E. Forsellini, R. Graziani, and G. Marangoni, *Inorg. Nucl. Chem. Lett.*, **10**, 1045 (1974).
(4) J. Albertsson and I. Elding, *Acta Crystallogr., Sect. B*, **B34**, 1460 (1977).
(5) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, *Acta Crystallogr., Sect. B*, **B30**, 2613 (1974).
(6) L. A. Aslanov, I. K. Abdul'miner, M. A. Porai-Koshits, and V. I. Ivanov, *Dokl. Akad. Nauk SSSR*, **205**, 343 (1972).
(7) R. J. Hill and C. E. F. Rickard, *J. Inorg. Nucl. Chem.*, **37**, 2481 (1975).
(8) E. J. Peterson, E. I. Onstott, and R. B. Von Dreele, *Acta Crystallogr., Sect. B*, **B35**, 805 (1979).
(9) L. J. Guggenberger and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 7221 (1976).
(10) B. E. Robertson, *Inorg. Chem.*, **16**, 2735 (1977).
(11) W. A. Dollase, *Acta Crystallogr., Sect. A*, **A30**, 513 (1974).
(12) M. G. B. Drew, *Coord. Chem. Rev.*, **24**, 179 (1977).