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New Di- and Trinuclear Complexes of Ruthenium with Octahedra Joined on Faces or Edges. 5.[1] Further Study of Edge-Sharing Bioctahedral Complexes of the Type $Ru_2Cl_6(PR_3)_4$ (R = Et, Bu)

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The new compound $Ru_2Cl_6(PEt_3)_4$ (**2**) has been prepared. The EPR spectra for this and for $Ru_2Cl_6(PBu_3)_4$ (**1**) have been recorded in frozen CH_2Cl_2–toluene solution at 77 K. The g values are as follows: (**1**) $g'_1 = 2.49$, $g'_2 = 1.83$, $g_1 = 2.28$, $g_2 = 2.07$, $g_3 = 1.91$; (**2**) $g'_1 = 2.49$, $g'_2 = 1.65$, $g_1 = 2.31$, $g_2 = 2.06$, $g_3 = 1.80$. The primed g values are assigned to the quasi-axial Ru^{III} center by comparison with data for discrete $[trans\text{-}RuCl_4(PR_3)_2]^-$ ions. These results support the view previously based on structural and magnetic susceptibility evidence for **1** that the two ruthenium atoms in these molecules are not bonded to each other nor even significantly coupled.

Introduction

Several years ago we reported crystallographic and magnetic susceptibility data for the compound $Ru_2Cl_6(PBu_3)_4$ (**1**) (Bu = $CH_3CH_2CH_2CH_2$–).[2] From the long Ru–Ru separation, 3.733 Å, other structural characteristics, and the magnetic properties (2.14 μ_B/Ru), it was concluded that there is no bond between the ruthenium atoms and probably not even much magnetic interaction. This result was somewhat surprising in view of the capability of the two d^5 Ru^{III} atoms to form a single bond. It was also in contrast to the case of $Ru_2Cl_6(dmpm)_2$,[3] where a Ru–Ru distance of 2.93 Å was found and the compound is diamagnetic.

To further validate our conclusion concerning the essential independence of the metal atoms in **1** and to see if this situation would be true for $Ru_2Cl_6(PR_3)_4$ compounds in general and in solution as well as in the crystalline state, we have made EPR measurements on **1** and also on $Ru_2Cl_6(PEt_3)_4$ (**2**).

Experimental Procedures

Compound **2** is difficult to obtain in both good yield and high purity. In comparison to **1**, where the tendency to lose one phosphine ligand and form $Ru_2Cl_6(PBu_3)_3$ is relatively low, compound **2** is very prone to expel one PEt_3 ligand. The following procedure was used to obtain a moderate yield of moderately pure **2**. $RuCl_3 \cdot H_2O$, 0.60 g (2.33 mmol), was dissolved in 3 mL of ethanol, and 0.67 g (5.65 mmol) of PEt_3 was added. This mixture was stirred for 2 h and then left undisturbed for 3 days at room temperature. A brown crystalline solid which had formed was separated by filtration, washed with ethanol (2 × 5 mL), and dried either in air or under vacuum. The yield was 0.44 g. A solution in CH_2Cl_2 showed electronic absorption bands at 335, 410, and 475 nm (cf. 340, 420, and 505 nm for **1**[2]) but also a weak broad hump at 830–840 nm, which shows that some $Ru_3Cl_8(PEt_3)_4$ was present as well. Since this compound is diamagnetic and EPR silent, its presence was not unduly deleterious. All attempts to purify **2** by recrystallization led to the formation of crystalline $Ru_2Cl_6(PEt_3)_3$, whose properties have been described previously.[4]

The EPR spectra of **1** and **2** were recorded on frozen CH_2Cl_2–toluene solutions at 77 K using an IBM Instruments, Inc., ER200D-SRC spectrometer equipped with a Bruker ER082(155/45) magnet. The results are shown in Figure 1.

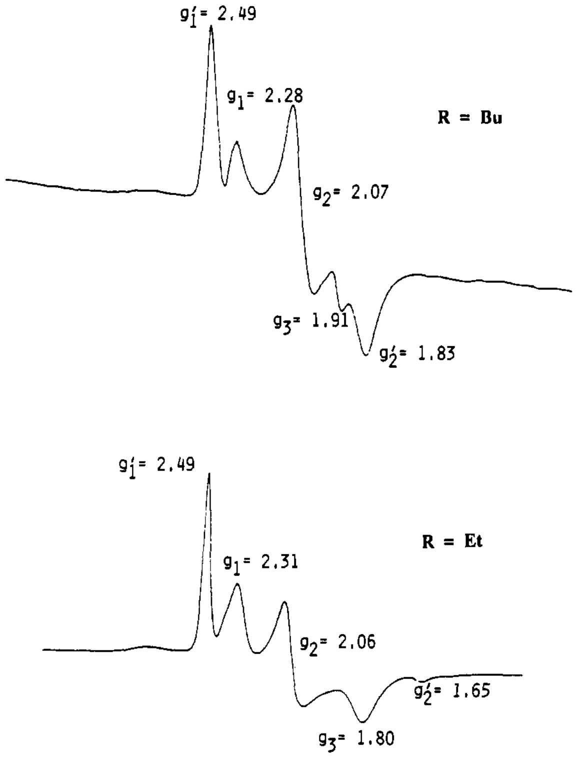
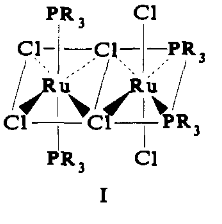


Figure 1. EPR spectra of frozen CH_2Cl_2–toluene solutions of $Ru_2Cl_6(PR_3)_4$, R = Bu (**1**) and Et (**2**), at 77 K.

Results and Conclusions

It must first be recalled that the structure of **1** is known (and that of **2** presumed) to be as shown schematically in I. This means that the two ruthenium centers are not equivalent. One of them is in a quasi-axial environment, while the other has a truly rhombic *cis,cis,trans*-$Ru(\mu\text{-}Cl_2)(PEt_3)_2Cl_2$ coordination. On this basis the five-line pattern observed in the EPR spectra of both compounds is readily interpretable. Two signals are due to the quasi-axial Ru^{III}, and the other three are due to the rhombic Ru^{III}. The fact that all these signals are in the normal range and have normal widths shows that the interaction between the two Ru atoms in each molecule is negligible.

The detailed assignment of individual signals to the appropriate type of Ru^{III} center can be made by reference to prior data on



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axial $[RuCl_4(PR_3)_2]^-$ ions. It is known that for R = Et such an anion has $g_1 = 2.51$ and $g_2 = 1.64$,[5] while for R = Bu the corresponding *g* values are $g_1 = 2.42$ and $g_2 = 1.58$.[4] Thus, the assignments given in Figure 1 (where g'_1 and g'_2 are for the quasi-axial Ru^{III} and g_1, g_2, and g_3 are for the rhombic Ru^{III}) follow straightforwardly.

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Registry No. **1**, 119719-52-7; **2**, 136676-24-9.

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Reaction of *trans,trans*-WH(CO)$_2$(NO)(PR$_3$)$_2$ with Lewis Acidic Boron Compounds. X-ray Structure of *trans*-W(η^2-BH$_4$)(CO)(NO)(PMe$_3$)$_2$

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Reaction of the basic hydrides *trans,trans*-WH(CO)$_2$(NO)(PR$_3$)$_2$ (R = Et, Me, Ph, OiPr) with BH$_3$·L (L = THF or SMe$_2$) yields air-sensitive *trans*-W(η^2-BH$_4$)(CO)(NO)(PR$_3$)$_2$ as the main product, whereas the more acidic hydrides (R = OMe, OPh) do not yield such a borohydride. The compounds W(η^2-BH$_4$)(CO)(NO)(PR$_3$)$_2$ are unstable with respect to elimination of BH$_3$·PR$_3$ and could therefore only be characterized by spectroscopic methods. However, we succeeded in growing crystals of W(η^2-BH$_4$)(CO)(NO)(PMe$_3$)$_2$, which were studied by X-ray diffractive methods: space group $Pna2_1$, $a = 10.313$ (1) Å, $b = 14.182$ (2) Å, $c = 10.771$ (2) Å, $Z = 4$, $R = 0.0287$, and $R_w = 0.0289$ for 1167 reflections with $F > 6\sigma(F)$.

Introduction

We have shown that the nitrosyl ligand in complexes of the type *trans,trans*-WH(CO)$_2$(NO)(PR$_3$)$_2$ causes a profound hydridic, i.e. basic, polarization of the trans-NO-positioned tungsten–hydride bond.[1] This is expressed in reactions of these complexes with mild acids like acetic acid and phenol, which result in facile elimination of dihydrogen. We have also shown that the hydridic character of these complexes can be further tuned by variation of the two cis-positioned phosphorus ligands.[2] Strongly σ-donating phosphines (PEt$_3$, PMe$_3$) were found to given more basic hydrides, whereas a strongly π-accepting phosphite, like P(OPh)$_3$, gave a more acidic complex. Moreover, we were able to quantify the reactivity of the W–H bond, by correlating it to the ν(W–H) stretching frequency, which in turn could be correlated to Tolman's electronic parameter of the phosphorus ligands.[3] We were interested whether the hydridic character of WH(CO)$_2$(NO)(PR$_3$)$_2$ was also expressed in its behavior toward Lewis acids and therefore decided to investigate its reactivity toward homoleptic boron compounds.

Experimental Section

IR spectra were obtained on a Biorad FTS-45 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini 200 spectrometer, ^{31}P NMR on a Varian XL-200 spectrometer, and ^{11}B on a Bruker AM-400-WB spectrometer. All reactions and manipulations were carried out under an atmosphere of dry nitrogen with freshly distilled solvents. WH(CO)$_2$(NO)(PR$_3$)$_2$ complexes with R = Et,[2] Me,[2] Ph,[4] OMe,[5] OiPr,[5] and OPh[5] were synthesized according to published methods.

Reaction of WH(CO)$_2$(NO)(PR$_3$)$_2$ with BH$_3$·L (L = THF, SMe$_2$). In a typical procedure, an orange solution of 0.2 mmol of the tungsten hydride in hexane (THF or toluene was used for R = Ph and OPh) was cooled to −80 °C and 1.5–2 equiv of either BH$_3$·THF (1 M in THF) or BH$_3$·SMe$_2$ (1 M in CH$_2$Cl$_2$) were added. When the temperature was slowly raised to +20 °C, the clear reaction mixture turns red for R = Ph and OiPr and violet for R = Me and Et between −20 and −10 °C,

Table I. Crystal Data for W(η^2-BH$_4$)(CO)(NO)(PMe$_3$)$_2$

formula	C$_7$H$_{22}$BNO$_2$P$_2$W
mol wt	408.9
cryst dimens, mm	0.3 × 0.3 × 0.4
cryst syst	orthorhombic
space group	$Pna2_1$
a, Å	10.313 (1)
b, Å	14.182 (2)
c, Å	10.771 (2)
V, Å^3	1575.2 (4)
Z	4
ρ(calcd), g cm^{-3}	1.724
μ, cm^{-1}	76.75
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite
data collcn T, K	233
index ranges	$-3 \le h \le 12$, $-4 \le k \le 17$, $-13 \le l \le 12$
θ range, deg	$1.0 \le \theta \le 26.0$
scan type	2θ-θ
no. of collcd reflcns	1585
no. of indep reflcns	1452
no. of obsd reflcns	1167 ($F > 6\sigma(F)$)
R, R_w	0.0287, 0.0289

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of W(η^2-BH$_4$)(CO)(NO)(PMe$_3$)$_2$ (Except Those for the C-Bound H's)

atom	x	y	z	U(eq)
W	0.20336 (4)	0.97477 (3)	0	0.0470 (1)
P1	0.0094 (3)	0.8737 (3)	0.002 (2)	0.062 (1)
P2	0.3831 (4)	1.0907 (2)	−0.000 (1)	0.063 (1)
O1	0.328 (4)	0.877 (3)	−0.213 (3)	0.14 (1)
O2	0.317 (3)	0.850 (2)	0.210 (3)	0.085 (8)
N	0.278 (2)	0.912 (2)	−0.119 (2)	0.073 (8)
C1	0.276 (3)	0.898 (2)	0.130 (4)	0.08 (1)
C2	−0.104 (4)	0.902 (2)	0.125 (3)	0.10 (1)
C3	−0.085 (3)	0.868 (2)	−0.142 (3)	0.09 (1)
C4	0.048 (2)	0.751 (1)	−0.018 (4)	0.073 (9)
C5	0.395 (5)	1.163 (4)	−0.132 (5)	0.08 (1)
C6	0.380 (5)	1.176 (4)	0.135 (5)	0.08 (1)
C7	0.540 (1)	1.039 (1)	−0.010 (6)	0.090 (9)
B	0.068 (2)	1.108 (1)	0.024 (4)	0.10 (1)
H1B	0.112 (8)	1.191 (5)	0.01 (1)	0.08
H2B	0.141 (8)	1.064 (8)	0.099 (9)	0.08
H3B	0.067 (9)	1.066 (9)	−0.079 (9)	0.08
H4B	−0.045 (7)	1.112 (6)	0.068 (9)	0.08

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