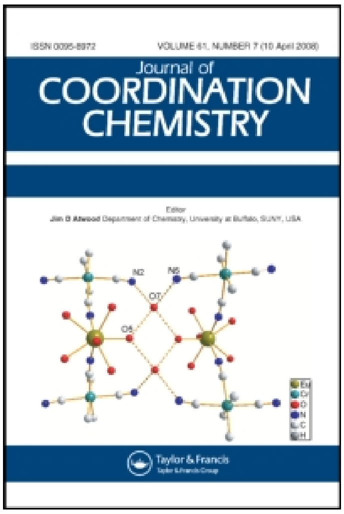

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RUTHENIUM(II) AND OSMIUM(II) COMPLEXES OF TRICYCLOHEXYLPHOSPHINE

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RUTHENIUM(II) AND OSMIUM(II) COMPLEXES OF TRICYCLOHEXYLPHOSPHINE

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The structures of the five-coordinate compounds $RuCl_2(CO)(PCy_3)_2$ and $OsHCl(CO)(PCy_3)_2$ are discussed and the electronic spectra of these types of compounds reported. The preparation and properties of the complexes $MHCl(CO)(PCy_3)_2L$ where L = acetylene or phenylacetylene. M = Ru or Os and PCy_3 = tricyclohexylphosphine are described.

INTRODUCTION

The complexes $MHCl(CO)(PCy_3)_2$ show coordinatively unsaturated behaviour and activate small molecules such as CS_2, CO, SO_2, $R_2C = CR_2$ and O_2.[1,2] $RuCl_2(CO)(PCy_3)_2$ reacts with CO and cyanoolefins.[3,4] These types of complexes have five coordinate structures. The trigonal bipyramid (TBP) and the square pyramid (SPY) geometries have particular interest in structures with simple coordination numbers because of the non-equivalence of all positions. This results in two sets of bonds with considerably different properties.[5] Repulsion between the two sets of ligands indicates that for ligands of the same sort the TBP arrangement is the most favoured and for the SPY structure the most stable arrangement is the structure with the angle $L_{axial}M\,L_{equatorial} = 104°$.[6] A good possibility for strong *n*-back bonding exists in the regular square-pyramidal configuration.[7]

It thus seemed of interest to examine the different structures of $OsHCl(CO)(PCy_3)_2$[8] and $RuCl_2(CO)(PCy_3)_2$.[9] In addition this paper reports the electronic spectra of $MHX(CO)(PCy_3)_2$ with M = Ru or Os and X = Cl or Br and of $RuCl_2(CO)(PCy_3)_2$ and the reactions of acetylene and phenylacetylene with these coordinatively unsaturated compounds.

EXPERIMENTAL

Materials

$MH(CO)X(PCy_3)_2$ and $RuCl_2(CO)(PCy_3)_2$ were prepared as previously described.[3,10] *Preparation of the compounds $MHX(CO)(PCy_3)_2L$ with L = acetylene or phenylacetylene*

Acetylene gas was passed through a solution of 0.03 mmol $MHCl(CO)(PCy_3)_2$ in 5 cm^3 of toluene during a half hour at room temperature. To this solution was added 5 cm^3 of *n*-hexane. After evaporating the mixture in a nitrogen/acetylene atmosphere the product was dried under vacuum. The reaction with phenylacetylene was performed in a similar way. However, instead of passing acetylene gas 0.2 cm^3 of phenylacetylene was added under a nitrogen atmosphere.

The analyses of the compounds prepared are given in Table I.

TABLE I
Analysis data for the complexes.

Complex	Colour	C%	H%
$OsHCl(CO)(PCy_3)_2(C_2H_2)$	rose	55.27(55.66)[a]	8.22(8.26)
$OsHCl(CO)(PCy_3)_2(C_8H_6)$	purple	59.23(58.90)	8.25(8.02)
$RuHCl(CO)(PCy_3)_2(C_2H_2)$	yellow	62.19(62.25)	9.26(9.24)
$RuHCl(CO)(PCy_3)_2(C_8H_6)$	red	66.45(65.23)	8.50(8.88)

[a] Theoretical values are given in parentheses.

Physical measurements

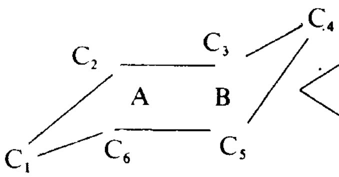
A Perkin-Elmer 283 infrared spectrophotometer was used for obtaining spectral data in the 4000–200 cm^{-1} range employing the caesium iodide pellet technique. Electronic spectra were recorded using a Perkin-Elmer 555 spectrophotometer.

RESULTS AND DISCUSSION

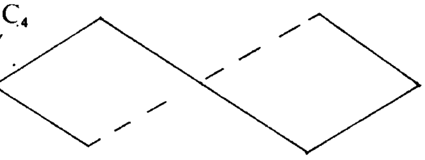
The structure determination of $OsHCl(CO)(PCy_3)_2$ shows the osmium atom, the two phosphorous atoms, the chlorine atom and the carbonyl group in the one plane.[8] The presence of the hydrido ion has been proven by different spectroscopic techniques.[10,11,12] The isotropic temperature factors of the carbon atoms of the cyclohexyl rings with the values U = 0.04–0.07(1) Å^2, and the anisotropic factors of the phosphorous atom $U_{11} = 0.035(4)$, $U_{22} = 0.038(4)$, $U_{33} = 0.034(4)$, $U_{12} = 0.018(4)$, $U_{13} = -0.005(4)$ and $U_{23} = 0.0001(35)$ lie within the expected range.

These results are the first example of a square-pyramidal structure with the metal atom lying in the basal square. Until now such an arrangement has never actually been observed with certainty. Probably the closest cases are the 1:1 adducts of stable square-planar d^8 systems, where the apical ligand exerts only a small pertubation upon the practically unchanged planar quadratic unit[13] and the complexes pentakis (phenylisocyanide)cobalt(II) perchlorate[14] and pentakis(2-imidazolidinone) copper(II) perchlorate.[15]

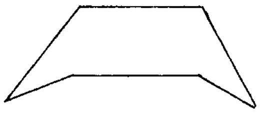
The hydrido compounds showed hydrogen/deuterium exchange of the hydrogen atoms of the cyclohexyl rings,[10,11] indicating the formation of a metal carbon bond. During the deuteration, the cyclohexyl rings may exist in the chair, boat or twist-boat conformation. It is therefore of interest to see which of these conformations the cyclohexyl rings have and to examine any deviations from the ideal. For distinguishing between the different conformations the angle C_1-A-C_4, where A is midway between C_2-C_6, is useful.



chair



twist-boat



boat

In the ideal chair, boat or twist-boat conformation the angle C_1-A-C_4 is 145°, 106° and 180°, respectively. The angles as calculated from X-ray data, given in Table II, clearly

TABLE II
The angle C_1-A-C_4 in the cyclohexylrings of the complexes.

Complexes	Angle C_1-A-C_4	Cyclohexylring bonded to[a]
$OsHCl(CO)(PCy_3)_2$	148(4)	C_5
	145(4)	C_8
	145(4)	C_{14}
$RuCl_2(CO)(PCy_3)_2$	150(3)	C_{13}
	146(2)	C_7
	145(2)	C_1
	148(3)	C_{25}
	178(4)	C_{31}
	149(2)	C_{19}

[a] for the notation see refs 8 and 9.

show that the rings in the $OsHCl(CO)(PCy_3)_2$ are in the chair conformation. The sum of the vectors C_1–A and C_4–B, where B is midway between C_3 and C_5, is zero, which is also in agreement with the chair conformation. A significant deviation of the rings from the chair conformation is not observed. An influence of the apical hydrido group on the positions of the equatorial ligands is not found. A bending of the basal ligands from the central atom has been observed in those compounds in which, instead of the hydrido ion, a phosphine[16] of a carbonyl acts as the axial ligand. It is generally found that the hydrido group has a large influence on the *trans* ligand,[17] however the influence on the *cis* ligands is small but in such compounds the *cis* ligands do bend towards the hydrido ion.[17,18]

$RuCl_2(CO)(PCy_3)_2$ has a square-pyramidal structure with the two phosphine ligands in a *trans* position, the carbonyl ligand at the apical site and an average axial ligand-ruthenium-basal ligand angle of 95.5(9)°.[9] One characteristic is the short axial carbonyl-ruthenium distance of 1.705(26) Å,[9] comparable with the short axial phosphine ruthenium distance 2.230(8)Å in $RnCl_2(PPh_3)_3$,[14] thus indicating a strong bond to the carbonyl group. In $RuCl_2(CO)(PCy)_3)_2$ there is a short contact distance involving the central atom and one of the hydrogen atoms of the cyclohexyl rings.[9] This short distance of 2.3(1) Å[9] results in a small ruthenium phosphorous carbon angle of 99.1(7)°,[9]. The average angle with the other cyclohexyl rings is 115.6(7)° and in $OsHCl(CO)(PCy_3)_2$[8] the angles lie in the 112.6–114.1(8)° range.

TABLE III
Electronic spectral data for the complexes

Complex	Medium	Observed bands[a]		molar extinction coefficient
		(nm)	(10^{-3} cm^{-1})	($\times 10^{-2}$) (M^{-1} cm^{-1})
$OsHCl(CO)(PCy_3)_2$	toluene	488[sh]	20.5	3
		424[sh]	23.6	6
		370	27.0	10
$OsHBr(CO)(PCy_3)_2$	toluene	482	20.7	5
		364[sh]	27.5	6
		324	30.9	13
$RuHCl(CO)(PCy_3)_2$	toluene	432[sh]	23.1	7
		384[sh]	26.0	10
		348	28.7	12
$RuCl_2(CO)(PCy_3)_2$	toluene	456[b]	21.6	6
		340	29.4	13

[a] sh = shoulder. [b] Bandwidth about 100 nm at half peak height.

The angle data, given in Table II, clearly indicate the chair conformation for 5 of the 6 cyclohexyl rings. The temperature factors of the carbon atoms in the chair conformations lie between U = 0.03–0.09(1) Å^2. However the temperature factors of the carbon atoms of the sixth ring are C_{31} = 0.07(1), C_{32} = 0.07(1), C_{33} = 0.12(1), C_{34} = 0.14(1), C_{35} = 0.13(1) and C_{36} = 0.07(1) Å^2 and the carbon atoms nearly lie in the very high energetic planar structure. These data suggest mobility and/or disorder in the ring, making a definite choice between the twist-boat, chair or boat conformations for this ring difficult. The ring with a short distance from one of the hydrogen atoms to the ruthenium atom showed no significant deviation from the chair conformation. The bending of the basal ligands from the ruthenium-CO vector may be caused by the carbonyl ligand in which the π-electron cloud could interact with them.

The visible spectra of the complexes studied in this work are given in Table III. Because of the large spin-orbit coupling, the presence of a carbonyl molecule and the distortion of the ligand field from true C_{4v} symmetry an unequivocal assignment of the bands is difficult. The absorption with the highest wavelength in the 20500–23100 cm^{-1} region may be the transition $^1B_2$ (d_{xij}) to $^1A_{1(d_z2)}$. This band shows a red shift from the ruthenium to the osmium complexes and may be explained by the lower energy of the d_z2 orbital caused by the larger splitting of d-orbitals in such osmium compounds.

TABLE IV
Infrared bands in the range 4000–200 cm^{-1}.

Compound	ν(CO)	ν(M-X)	δ(MCO)	Other bands
$OsHCl(CO)(PCy_3)_2(C_2H_2)$	1902s	285w	612m 600sh	2000w, 1024w
$OsHCl(CO)(PCy_3)_2(C_8H_6)$	1888s	278w 288w	557w 611w 598w	1595w, 1575w 690m, 921m
$RuHCl(CO)(PCy_3)_2(C_2H_2)$	1908s	270w	602m 550w	2024m, 955w
$RuHCl(CO)(PCy_3)_2(C_8H_6)$	1904s	280w	600m, 551m 595sh	1597m, 1577m, 691m

The compounds studied in this work are listed in Table I, together with their colours and analytical data. The most important infrared absorption bands are shown in Table IV. Toluene solutions of $MHCl(CO)(PCy_3)_2$ react rapidly at room temperature with acetylene or phenylacetylene with a change of colour. In contrast to the reaction of ethylene[2] with the hydridocarbonyl complex the acetylene and phenylacetylene reactions yield isolable pure products of the composition $MHCl(CO)(PCy_3)_2L$. The solutions do not lose acetylene or phenylacetylene on sweeping with nitrogen. The infrared spectra showed a slight increase of the ν(CO) and a decrease of the ν(M–Cl) as also has been observed in cyanoolefin complexes of ruthenium (II) and osmium (II).[4] The phenylacetylene compounds of the hydridocarbonyl complexes showed in the 1600 cm^{-1} region several bands assignable to ν(C=C) and δ(C–H) vibrations, indicating a shift difference of about 535 cm^{-1} compared with the free ligand (2120 cm^{-1}). A similar shift has been observed in the symmetric Pt complexes with dicyanoacetylene and phenylacetylene as ligands.[19] The reaction of excess phenylacetylene with $RuCl_2(CO)(PCy_3)_2$ or $RuHCl(CO)(PCy_3)_2$ resulted in products with elemental analyses corresponding to 3 to 4 mol of C_8H_6 per Ru. The infrared spectra showed new bands at about 1765 and 755 cm^{-1} and the bands at 1595 and 1575 cm^{-1} decreased in intensity. The absorption band in the 690 cm^{-1} region assigned to the phenyl group of the phenylacetylene ligand increased strongly in intensity and was split (690–698 cm^{-1}). The δ(MCO) mode in the 600 cm^{-1} region also showed splitting. These results suggest oligomerisation of the phenylacetylene under the influence of the ruthenium complexes.

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