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CATIONIC RUTHENIUM HYDRIDO COMPLEXES CONTAINING *N*- AND *P*-DONOR LIGANDS. CRYSTAL STRUCTURE OF CARBONYLHYDRIDO(1,4-BIS(CYCLOHEXYL)-DIAZA-1,3-BUTADIENE)BIS-(METHYLDIPHENYLPHOSPHINE)RUTHENIUM(II) · PERCHLORATE

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Summary

A series of cationic complexes of the type $[Ru(CO)H(L_2)(PR_3)_2] \cdot ClO_4$ (L_2 = 2py, bpy, phen, Cy-DAB) have been obtained by reaction of $Ru(CO)ClH(PR_3)_3$ (R = Ph, $4\text{-}MeC_6H_4$; $R_3 = MePh_2$) with the *N*-donor ligands pyridine (py), 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or 1,4-bis(cyclohexyl)-diaza-1,3-butadiene (Cy-DAB).

The complexes have been identified by elemental analysis, ^1H NMR and IR spectroscopy. The structure of $[Ru(CO)H(Cy\text{-}DAB)(PMePh_2)_2] \cdot ClO_4$ has been determined by an X-ray diffraction study, confirming that the Cl and one PR_3 ligand have been replaced by one molecule of Cy-DAB. The Ru atom is octahedrally coordinated with H, CO and Cy-DAB in the equatorial plane and the two $PMePh_2$ molecules in the axial positions.

The catalytic properties of some of the compounds in hydrogenation of 1-hexene have been studied.

Introduction

Reports of ruthenium hydrido complexes containing *N*- and *P*-donor ligands are relatively scarce. It seemed to us that partial substitution of phosphine molecules by *N*-donor molecules in ruthenium hydrido complexes of the type $RuHX(PR_3)_nL_m$ might significantly change the reactivity of the Ru–H bond and hence the catalytic properties. Complexes of general formula $Ru(CO)ClH(PR_3)_3$ are appropriate for such a study, and their substitution chemistry is relatively undeveloped; only the reactions of $Ru(CO)ClH(PPh_3)_3$ with arenediazonium compounds [1], diarylcarbodiimides [2], pyridine-2-thiolate derivates [3], 2-acylpyridines [4], 2-amino-pyridines and -pyrimidines [5], acetonitrile [6] and substituted pyrazoles and bipyrazoles [7], to give insertion or substitution products, have been reported.

We describe here the reactions of pyridine (py), 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and 1,4-bis(cyclohexyl)-diaza-1,3-butadiene (Cy-DAB) with $Ru(CO)ClH(PR_3)_3$ complexes ($R = Ph$, $4\text{-}MeC_6H_4$; $R_3 = MePh_2$).

Results and discussion

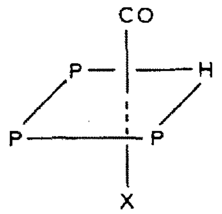
The reactions of $Ru(CO)ClH(PR_3)_3$ ($R = Ph$, $4\text{-}MeC_6H_4$; $R_3 = MePh_2$) with *N*-donor ligands yield cationic complexes of the type $[Ru(CO)H(L_2)(PR_3)_3] \cdot ClO_4$ (L_2 = 2py, bpy, phen, Cy-DAB), which can be regarded as resulting from substitution of Cl and one PR_3 molecule by one (L_2 = bpy, phen, Cy-DAB) or two (L = py) molecules of the *N*-donor ligands. Table 1 lists the new complexes obtained, and presents some of their physical properties.

The conductance values in nitromethane fall in the range 70–84 Ω^{-1} cm^2 mol^{-1} and are lower than those corresponding to a 1 : 1 electrolyte [8], as expected in view of the large size of the complex cation.

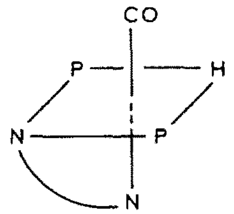
For all these complexes there is an increase in the $\nu(CO)$ stretching frequency with respect to those for the starting compounds (1920vs, 1900sh cm^{-1} for $Ru(CO)ClH(PPh_3)_3$; 1915vs, 1905sh cm^{-1} for $Ru(CO)ClH[P(p\text{-tolyl})_3]_3$ and 1915vs, 1900sh cm^{-1} for $Ru(CO)ClH(PMePh_2)_3$). For complexes derived by a simple substitution, such as $Ru(CO)ClH(PCy_3)_2(py)$ [9], the observed decrease of this $\nu(CO)$ frequency with respect to the starting complex was explained in terms of the assumption of the strong σ-donor and weak π-back-acceptor ability of the pyridine ligand, which results in an increase in the basicity of the metal. In our case the presence of a formal positive charge on the ruthenium atom increases the acid character of the metal, and this weakens the π-back-bonding to the ligand with a consequent increase in $\nu(CO)$. A similar increase has been observed for the analogous complex $[Ru(CO)H(MeCN)_2(PPh_3)_2]^+$ (1960vs cm^{-1}). The existence of single $\nu(Cl\text{–}O)$ and $\delta(OClO)$ bands corresponds to a T_d symmetry of the ClO_4^- anion.

Table 2 gives the ^1H NMR spectral data for the complexes. As in other transition-metal hydride complexes [10], the chemical shifts of the hydridic hydrogens are large, and the resonances are split by coupling to the phosphorus nuclei. The resonance signals for the hydridic hydrogens of the starting complexes consist of a doublet of triplets at δ ca. −6.8 ppm, with strong coupling to the *trans*-phosphorus atom ($J(HP)$ 108 Hz) and weaker coupling to the *cis*-phosphorus atoms ($J(HP)$ 22 Hz). This corresponds to the configuration **1** for these complexes. The signals of the hydridic hydrogens of the substituted complexes with *N*-donor ligands are single triplets at δ ca. −11 ppm, with $J(HP)$ 20 Hz, corresponding to the coupling with two *cis*-phosphorus atoms, which is in agreement with the configuration **2**.

The signals to the methyl groups of the $PMePh_2$ ligands in the complexes IX, X, XI and XII show virtual coupling with the phosphorus nuclei, similar to that previously described [10]. The starting complex $Ru(CO)ClH(PMePh_2)_3$ gives one triplet at δ 1.90 ppm, $J(HP)$ 3.9 Hz,6H and a doublet at δ 1.55 ppm, $J(HP)$ 6.6 Hz,3H. In the substituted *N*-donor complexes gives only one triplet, which confirms the configuration **2**. This configuration has been established unequivocally for



(1)



(2)

$[Ru(CO)H(Cy\text{-}DAB)(PMePh_2)_2] \cdot ClO_4$, by an X-ray crystal structure determination.

The large displacement of the hydridic hydrogen signals towards the higher field values with respect to the corresponding starting complexes (Table 2) is indicative of a greater shield at the hydridic hydrogen as consequence of the replacement of a phosphine molecule by a poorer π-acceptor ligand, which weakens the Ru–H bond. The ν(Ru–H) stretching frequency, which for the starting complexes appears at ca. 2010 cm^{-1}, is shifted towards the lower frequencies in the substituted complexes and becomes obscured by the strong ν(CO) absorption. This is consistent a with weakening of the Ru–H bond in the substituted complexes. There is a correlation between the π-acceptor capacity of the ligands and the extent of displacement of the hydridic hydrogen signal relative to that of the starting complex, the displacement

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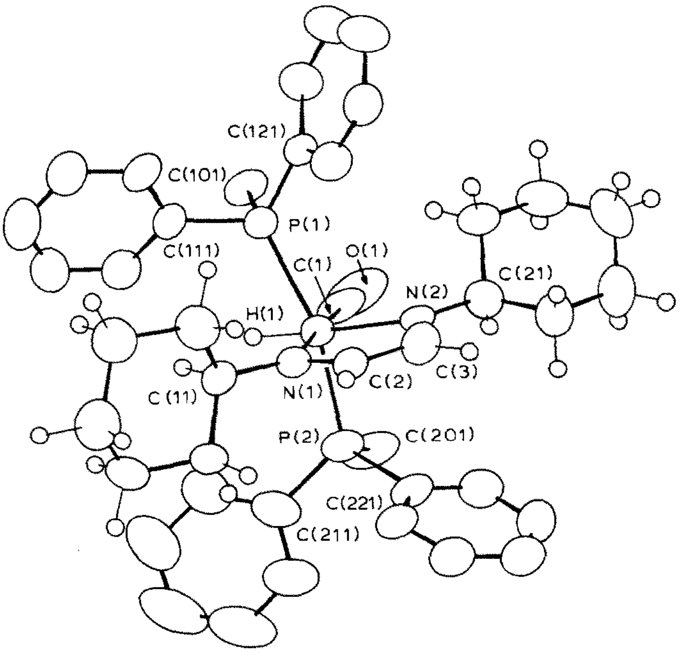

Fig. 1. ORTEP [16] drawing of the $Ru(CO)H(Cy\text{-}DAB)(PMePh_2)$ cation, showing the octahedral coordination around the Ru atom.

TABLE 1

ANALYTICAL, CONDUCTANCE AND INFRARED DATA FOR THE COMPLEXES

Compound		Colour	Analyses (Found (calc) (%))			Λ (Ω^{-1} cm^2 mol^{-1})	IR (cm^{-1})			
			C	H	N		ν(CO)	ν(C=N)	ν(ClO)	δ(OClO)
$[Ru(CO)H(L_2)(PPh_3)_2]ClO_4$										
L = py	(I)	pale-yellow	61.35 (61.87)	4.87 (4.52)	2.95 (3.07)	84.38	1934vs	1603m	1085vs	620m
L_2 = bpy	(II)	yellow-orange	61.80 (62.01)	4.39 (4.31)	3.02 (3.07)	76.52	1950vs	1605m	1092vs	625m
L_2 = phen	(III)	yellow	62.59 (62.99)	4.37 (4.20)	2.98 (2.99)	81.80	1948vs	1620m	1080vs	618m
L_2 = Cy-DAB	(IV)	orange	61.90 (62.86)	5.92 (5.68)	2.70 (2.87)	75.95	1942vs		1080vs	630m
$[Ru(CO)H(L_2)\{P(p\text{-}tolyl)_3\}_2]ClO_4$										
L = py	(V)	yellow-lemon	62.95 (63.88)	5.40 (5.36)	2.77 (2.81)	68.96	1930vs	1608m	1095vs	630m
L_2 = bpy	(VI)	yellow-lemon	63.61 (64.01)	5.12 (5.16)	2.88 (2.81)	69.57	1945vs	1598m	1084vs	625m
L_2 = phen	(VII)	yellow	64.15 (64.86)	5.25 (5.04)	2.80 (2.75)	74.38	1942vs	1606m	1092vs	632m
L_2 = Cy-DAB	(VIII)	orange	64.28 (64.67)	6.28 (6.37)	2.52 (2.64)	70.33	1938vs		1080vs	625m
$[Ru(CO)H(L_2)(PMePh_2)_2]ClO_4$										
L = py	(IX)	yellow	55.70 (56.38)	4.90 (4.73)	3.40 (3.55)	77.60	1935vs	1605m	1098vs	618m
L_2 = bpy	(X)	yellow-orange	55.87 (56.52)	4.56 (4.48)	3.35 (3.56)	72.85	1940vs	1598m	1084vs	625m
L_2 = phen	(XI)	orange	57.10 (57.81)	4.42 (4.35)	3.40 (3.45)	79.35	1945vs	1600m	1090vs	630m
L_2 = Cy-DAB	(XII)	red-orange	58.01 (57.91)	6.35 (6.04)	3.13 (3.29)	72.45	1940vs		1090vs	620m

TABLE 2

^{1}H NMR SPECTRA FOR THE COMPLEXES (δ (ppm), J (Hz); TMS as int. standard, solvent DMSO-d_6)

Compound	Hydridic hydrogen	*N*-donor ligand	*P*-donor ligand
I	−12.10 (t,1H,J(PH) 19.5)	8.66 (dd,H$_\alpha$,4H), 8.16 (dd,H$_\gamma$,2H), 7.60 (dd,H$_\beta$,4H) (J(H$_\alpha$–H$_\beta$) 6; J(H$_\alpha$–H$_\gamma$) 1.5; J(H$_\beta$–H$_\gamma$) 8)	7.46–7.20 (m,30H,6Ph)
II	−11.40 (t,1H,J(PH) 19.2)	8.96(m), 8.16(m), 7.86(m), 7.73 (m,8H bpy)	7.38–7.15 (m,30H,6Ph)
III	−11.10 (t,1H,J(PH) 18)	8.48 (dd,H$_\alpha$,2H), 8.28 (dd,H$_\gamma$,2H), 7.96 (s,H$_\epsilon$,2H), 7.72 (dd,Hβ,2H) (J(H$_\alpha$–H$_\beta$ 3, J(H$_\alpha$–H$_\gamma$) 1.5; J(H$_\beta$–H$_\gamma$) 6)	7.30–7.05 (m,30H,6Ph)
IV	−10.68 (t,1H,J(PH) 21)	8.05 (s,2H,iminic proton), 2.93 (m,2H,H(1),c-hexyl), 1.45–0.93 (20H,c-hexyl)	7.60–7.37 (m,30H,6Ph)
V	−11.93 (t,1H,J(PH) 20)	8.90 (dd,H$_\alpha$,4H), 8.20 (dd,H$_\gamma$,2H), 7.65 (dd,H$_\beta$,4H) (J(H$_\alpha$–H$_\beta$) 7; J(H$_\alpha$–H$_\gamma$) 1; J(H$_\beta$–H$_\gamma$) 8.5)	2.35 (s,18H,6Me) 7.50–7.30 (m,24H,6*p*-tolyl)
VI	−11.30 (t,1H,J(PH) 20)	8.85(m), 8.30(m), 8.11(m), 7.85 (m,8H,bpy)	2.38 (s,18H,6Me) 7.35–7.00 (m,24H,6*p*-tolyl)
VII	−11.00 (t,1H,J(PH) 19.8)	8.60 (dd,H$_\alpha$,2H), 8.35 (dd,H$_\gamma$,2H), 8.00 (s,H$_\epsilon$,2H), 7.70 (dd,H$_\beta$,2H) (J(H$_\alpha$–H$_\beta$) 3; J(H$_\alpha$–H$_\gamma$) 2; J(H$_\beta$–H$_\gamma$) 6)	2.30 (s,18H,6Me) 7.40–7.15 (m,24H,6*p*-tolyl)
VIII	−10.80 (t,1H,J(PH) 19.2)	8.07 (s,2H,iminic proton), 2.95 (m,2H,H(1),c-hexyl) 1.50–0.98 (20H,c-hexyl)	2.33 (s,18H,6Me) 7.37–7.05 (m,24H,6*p*-tolyl)
IX	−12.02 (t,1H,J(PH) 18.6)	8.80 (dd,H$_\alpha$,4H), 8.25 (dd,H$_\gamma$,2H), 7.55 (dd,H$_\beta$,4H) (J(H$_\alpha$–H$_\beta$) 6.3; J(H$_\alpha$–H$_\gamma$) 1.8; J(H$_\beta$–H$_\gamma$) 7.6)	1.78 (t,6H,J(PH) 3,2Me) 7.48–7.30 (m,20H,4Ph)
X	−11.35 (t,1H,J(PH) 19.8)	8.50(m), 8.20(m), 8.01(m), 7.90(m,8H bpy)	1.73 (t,6H,J(PH) 3.2,2Me) 7.35–7.00 (m,20H,4Ph)
XI	−11.06 (t,1H,J(PH) 20)	8.50 (dd,H$_\alpha$,2H), 8.35 (dd,H$_\gamma$,2H), 8.08 (s,H$_\epsilon$,2H), 7.74 (dd,H$_\beta$,2H) (J(H$_\alpha$–H$_\beta$) 2.5; J(H$_\alpha$–H$_\gamma$) 1.3; J(H$_\beta$–H$_\gamma$) 6.3)	1.82 (t,6H,J(PH) 3,2Me) 7.40–7.25 (m,20H,4Ph)
XII	−10.36 (t,1H,J(PH) 20)	8.22 (s,2H,iminic proton), 3.08 (m,2H,H(1),c-hexyl) 1.57–1.05 (20H,c-hexyl)	1.84 (t,6H,J(PH) 3.2,2Me) 7.62–7.45 (m,20H,4Ph)

being larger for the poorer π-acceptor N ligands. Thus for $[Ru(CO)H(NCMe)_2(PPh_3)_2]ClO_4$ this signal is at δ −13.1 ppm and for $[RuH(CO)_2(PPh_3)_3]ClO_4$ is at δ −6.4 ppm [6]. The δ values of our complexes lie between those two values, but closer to that for the acetonitrile compound.

The catalytic properties of $[Ru(CO)H(py)_2(PPh_3)_2]ClO_4$ in the hydrogenation of 1-hexene under normal pressure and temperature, have been studied and compared with those of $Ru(CO)ClH(PPh_3)_3$. In both cases the maximum yield (12% for $[Ru(CO)H(py)_2(PPh_3)_2]\cdot ClO_4$ and 14% for $Ru(CO)ClH(PPh_3)_3$) is found for photochemical activation with UV-radiation.

The structure of $[Ru(CO)H(Cy\text{-}DAB)(PMePh_2)_2]\cdot ClO_4$

The crystal consists of $[Ru(CO)H(Cy\text{-}DAB)(PMePh_2)_2]^+$ cations and ClO_4^- anions which show no hydrogen-bond interaction. Table 3 lists the more relevant bond lengths and angles of the cation, which is represented in Fig. 1.

As deduced from the ^1H NMR data, the hydridic hydrogen is in a *cis* position with respect to the two $PMePh_2$ ligands. The interatomic distances involving the Ru atom are as expected and agree well with those observed in other complexes reported previously [7,11]. In the Cy-DAB moiety, the distances N(1)–C(2) (1.268(9) Å) and N(2)–C(3) (1.291(9) Å) correspond to double N=C bonds and do not deviate significantly from those for the free organic molecule (1.258(2) Å) [12].

The value of the angle P–Ru–P (162.4(1)°) indicates that the two Ru–P bonds are bent. From the bond angles listed in Table 3 it can be deduced that the bending is away from the Cy-DAB ligand and over towards the H ligand more than to the CO group.

TABLE 3

BOND DISTANCES (Å) AND ANGLES (°) FOR $[Ru(CO)H(Cy\text{-}DAB)(PMePh_2)_2]ClO_4$

Ru–P(1)	2.355(2)	P(2)–C(201)	1.848(8)
Ru–P(2)	2.362(2)	P(2)–C(211)	1.826(8)
Ru–N(1)	2.151(5)	P(2)–C(221)	1.811(9)
Ru–N(2)	2.149(6)	C(1)–O(1)	1.16(1)
Ru–C(1)	1.833(8)	N(1)–C(2)	1.268(9)
Ru–H(1)	1.29	N(1)–C(11)	1.487(9)
P(1)–C(101)	1.837(9)	N(2)–C(3)	1.291(9)
P(1)–C(111)	1.819(8)	N(2)–C(21)	1.479(9)
P(1)–C(121)	1.824(7)	C(2)–C(3)	1.44(1)

Mean C–C in phenyl rings 1.386(15)
Mean C–C in c-hex rings 1.522(13)

P(1)–Ru–P(2)	162.4(1)	P(2)–Ru–H(1)	94.5	Ru–N(1)–C(11)	127.2(5)
P(1)–Ru–N(1)	93.4(1)	N(1)–Ru–N(2)	75.6(2)	C(2)–N(1)–C(11)	118.6(6)
P(1)–Ru–N(2)	105.9(2)	N(1)–Ru–C(1)	175.1(3)	Ru–N(2)–C(3)	113.8(5)
P(1)–Ru–C(1)	87.6(2)	N(1)–Ru–H(1)	89	Ru–N(2)–C(21)	126.7(5)
P(1)–Ru–H(1)	69	N(2)–Ru–C(1)	99.5(3)	C(3)–N(2)–C(21)	119.0(6)
P(2)–Ru–N(1)	91.9(1)	N(2)–Ru–H(1)	163	N(1)–C(2)–C(3)	118.4(7)
P(2)–Ru–N(2)	91.6(2)	C(1)–Ru–H(1)	96	N(2)–C(3)–C(2)	117.2(7)
P(2)–Ru–C(1)	88.5(3)	Ru–N(1)–C(2)	114.2(4)	Ru–C(1)–O(1)	178.9(8)
Mean C–P–C	102.2(4)	Mean C–C–C in phenyl rings	120 (1)	Mean C–C–C in c-hex rings	110.8(7)

Experimental

The ^{1}H NMR spectra were recorded on a Bruker WM 360 spectrometer at 360 MHz; shifts are relative to TMS (0.00 ppm). IR spectra were recorded with a Perkin–Elmer 325 instrument using KBr disks. Elemental analyses were performed with a Hewlet–Packard CHN 185 microanalyser. Solvents were dried and distilled under nitrogen, and all operations were conducted under dry, oxygen-free nitrogen.

$Ru(CO)ClH(PPh_3)_3$ was prepared as previously described [13], and $Ru(CO)ClH(P(p\text{-tolyl})_3)_3$ and $Ru(CO)ClH(PMePh_2)_3$ were prepared similarly.

$[Ru(CO)H(py)_2(PPh_3)_2]ClO_4$ (I)

Pyridine (0.25 ml, solution 2 *M* in EtOH, 0.5 mmol) was added in a stoichiometric amount to a suspension of $Ru(CO)ClH(PPh_3)_3$ (200 mg, 0.2 mmol) in EtOH (25 ml). After 30 min stirring at 50°C the yellow solution was concentrated to 10 ml and $NaClO_4$ (26 mg, 0.2 mmol) was added. A yellow solid appeared and was washed with ethanol and diethyl ether (yield 70%). It was recrystallized from CH_2Cl_2/EtOH solution.

$[Ru(CO)H(bpy)(PPh_3)_2]ClO_4$ (II), $[Ru(CO)H(phen)(PPh_3)_2]ClO_4$ (III) and $[Ru(CO)H(Cy\text{-}DAB)(PPh_3)_2]ClO_4$ (IV) were prepared as I with yields of 73, 78% and 80%, respectively.

$[Ru(CO)H(py)_2\{P(4\text{-}Me\text{-}C_6H_4)_3\}_2]ClO_4$ (V)

Pyridine (0.25 ml, solution 2 *M* in EtOH, 0.5 mmol) was added to a suspension of $Ru(CO)ClH(P(p\text{-tolyl})_3)_3$ (216 mg, 0.2 mmol) in CH_2Cl_2/EtOH, 1/1 (30 ml). The solution was concentrated to 10 ml after 30 min stirring at 40°C and then $NaClO_4$ (26 mg, 0.2 mmol) was added. After concentration, n-hexane was added, and the yellow precipitate formed was washed with n-hexane and diethyl ether (yield 65%). It was recrystallized from EtOH/n-hexane solution.

$[Ru(CO)H(bpy)\{P(4\text{-}Me\text{-}C_6H_4)_3\}_2]ClO_4$ (VI), $[Ru(CO)H(phen)\{P(4\text{-}Me\text{-}C_6H_4)_3\}_2]ClO_4$ (VII) and *$[Ru(CO)H(Cy\text{-}DAB)\{P(4\text{-}Me\text{-}C_6H_4)_3\}_2]ClO_4$ (VIII)* were synthetized in the same way as V in yields of 65, 67 and 75%, respectively.

$[Ru(CO)H(py)_2(PMePh_2)_2]ClO_4$ (IX)

Pyridine (0.25 ml, solution 2 *M* in EtOH, 0.5 mmol) was added to a solution of $Ru(CO)ClH(PMePh_2)_3$ (150 mg, 0.2 mmol) in CH_2Cl_2/EtOH, 1/1 (30 ml). After 1 h stirring at 40°C the solution was concentrated to 10 ml and a white solid (50 mg), assumed to be $Ru(CO)ClH(PMePh_2)_3$, separated out. Addition of $NaClO_4$ (26 mg, 0.2 mmol) followed by of n-hexane gave a yellow solid, which was washed with n-hexane and diethyl ether (yield 55%). It was recrystallized from EtOH/n-hexane.

$[Ru(CO)H(bpy)(PMePh_2)_2]ClO_4$ (X), $[Ru(CO)H(phen)(PMePh_2)_2]ClO_4$ (XI) and $[Ru(CO)H(Cy\text{-}DAB)(PMePh_2)_2]ClO_4$ (XII) were prepared as IX with yields of 67, 58 and 65%, respectively. Recrystallization of the $[Ru(CO)H(Cy\text{-}DAB)(PMePh_2)_2]ClO_4$ from CH_2Cl_2/EtOH gave crystals suitable for the X-ray structure determination.

TABLE 4

ATOM COORDINATES FOR $[Ru(CO)H(Cy\text{-}DAB)(PMePh_2)_2]\cdot ClO_4$ (Thermal parameters as $U_{eq} = 1/3\Sigma[U_{ij}a_i^{\star}a_j^{\star}\mathbf{a}_i\mathbf{a}_j \cos(a_i a_j)] \times 10^4$)

Atom	x	y	z	U_{eq} (Å^2)
Ru	0.68206(6)	0.22789(3)	0.12627(3)	334(3)
P(1)	0.6187(2)	0.1330(1)	0.0561(1)	384(6)
P(2)	0.6806(2)	0.3191(1)	0.2029(1)	465(7)
N(1)	0.6757(6)	0.2974(3)	0.0432(3)	373(20)
N(2)	0.8802(6)	0.2461(3)	0.1207(3)	391(20)
C(1)	0.7024(9)	0.1685(4)	0.1976(4)	575(32)
O(1)	0.7151(9)	0.1301(4)	0.2420(3)	966(34)
C(2)	0.7848(7)	0.3192(4)	0.0350(3)	405(25)
C(3)	0.8973(7)	0.2934(4)	0.0785(4)	440(26)
C(11)	0.5600(7)	0.3205(4)	−0.0044(3)	426(25)
C(12)	0.5342(8)	0.3669(4)	0.0018(4)	557(30)
C(13)	0.4075(9)	0.4150(5)	−0.0450(5)	749(39)
C(14)	0.4102(10)	0.3963(5)	−0.1168(5)	740(39)
C(15)	0.4441(9)	0.3220(5)	−0.1241(4)	672(35)
C(16)	0.5703(8)	0.3037(4)	−0.0779(4)	542(29)
C(21)	0.9934(7)	0.2165(4)	0.1649(3)	429(25)
C(22)	1.1202(8)	0.2521(4)	0.1647(4)	565(30)
C(23)	1.2278(9)	0.2179(6)	0.2143(5)	724(38)
C(24)	1.2389(10)	0.1422(6)	0.1988(5)	764(41)
C(25)	1.1123(11)	0.1068(5)	0.1977(4)	703(38)
C(26)	1.0025(9)	0.1401(4)	0.1496(4)	570(31)
C(101)	0.5662(9)	0.0605(4)	0.1023(4)	579(32)
C(111)	0.7315(7)	0.0950(4)	0.0084(3)	410(24)
C(112)	0.7438(9)	0.0248(4)	−0.0005(5)	628(34)
C(113)	0.8280(11)	−0.0003(5)	−0.0400(6)	830(45)
C(114)	0.8995(10)	0.0440(6)	−0.0714(5)	771(42)
C(115)	0.8890(8)	0.1133(5)	−0.0629(4)	578(32)
C(116)	0.8056(8)	0.1394(4)	−0.0237(4)	497(28)
C(121)	0.4753(7)	0.1447(4)	−0.0077(4)	457(26)
C(122)	0.4701(8)	0.1276(4)	−0.0751(4)	558(31)
C(123)	0.3560(9)	0.1364(5)	−0.1211(5)	682(37)
C(124)	0.2480(10)	0.1621(6)	−0.1015(6)	799(42)
C(125)	0.2506(9)	0.1786(5)	−0.0345(6)	735(40)
C(126)	0.3630(8)	0.1704(4)	0.0118(4)	566(31)
C(201)	0.6944(11)	0.2908(5)	0.2911(4)	793(43)
C(211)	0.8099(8)	0.3814(4)	0.2048(4)	477(28)
C(212)	0.7971(8)	0.4330(4)	0.1561(4)	565(31)
C(213)	0.8946(10)	0.4794(5)	0.1551(5)	687(38)
C(214)	1.0056(10)	0.4751(5)	0.2003(6)	777(44)
C(215)	1.0210(10)	0.4238(6)	0.2484(6)	831(45)
C(216)	0.9236(10)	0.3757(5)	0.2500(5)	658(36)
C(221)	0.5418(9)	0.3748(5)	0.1935(5)	646(36)
C(222)	0.4287(10)	0.3603(5)	0.1499(6)	813(45)
C(223)	0.3250(12)	0.4059(8)	0.1409(9)	1244(74)
C(224)	0.3376(15)	0.4666(8)	0.1787(11)	1365(89)
C(225)	0.4469(17)	0.4808(7)	0.2222(8)	1173(73)
C(226)	0.5479(11)	0.4358(5)	0.2308(5)	845(47)
Cl	0.9986(3)	0.1722(1)	0.4021(1)	772(10)
O(2)	0.9532(10)	0.2276(6)	0.4303(5)	1443(36)
O(3)	0.9018(11)	0.1208(6)	0.3922(5)	1479(38)
O(4)	1.0819(18)	0.1704(9)	0.3634(9)	2601(79)
O(5)	1.0946(18)	0.1534(9)	0.4602(9)	2530(76)
H(1)	0.558	0.223	0.112	38

X-ray diffraction data

$C_{41}H_{51}N_2ClO_5P_2Ru$, $M = 850.34$, Monoclinic, $P2_1/c$, a 10.581(1), b 19.519(1), c 20.209(1) Å, β 100.20(1)°, U 4107.8 Å^3, $Z = 4$, D_x 1.37 g cm^{-3}, $F(000)$ 1768, λ(Cu-K_α) 1.5418 Å, μ(Cu-K_α) 48.7 cm^{-1}, crystal dimensions: $0.26 \times 0.10 \times 0.06$ mm. 6086 reflexions measured on a Philips diffractometer up to θ_{max} 60°. 1173 reflexions, with $I \leqslant 4\sigma(I)$ were considered unobserved. No absorption correction was applied. No crystal decay was observed for two reference reflexions measured every 90 min.

Structure solution and refinement

Atomic scattering factors for neutral atoms and anomalous dispersion factors, for Ru and Cl, were taken from International Tables for X-ray Crystallography [14]. Normal heavy atom procedures were followed by Fourier Synthesis. Full-matrix least-squares refinement was carried out. Unit weights were applied to every reflexion. A ΔF Fourier synthesis was calculated to determine the positions of the H atoms which were located in the vicinity of the calculated positions. The thermal motion was taken as anisotropic for all atoms except the oxygens of ClO_4^- which were refined isotropically and hydrogens which were fixed at the calculated positions except the hydrido hydrogen which was fixed at position found in the Fourier synthesis. A total of 449 parameters were varied. The refinement converged at $R = 0.062$ for observed reflexions only. Most of the calculations were performed with the 'XRAY-70' system of crystallographic programs [15]. The final atomic coordinates are collected in Table 4. Lists of structure factors and thermal parameters are available from the authors.

References

1 J.A. McCleverty, D. Seddon and R.W. Whiteley, J. Chem. Soc., Dalton Trans., (1975) 839.
2 L.D. Brown, S.D. Robinson, A. Schahajpal and J.A. Ibers, Inorg. Chem., 16 (1977) 2728.
3 P. Mura, B.G. Olby and S.D. Robinson, J. Chem. Soc., Dalton Trans., (1985) 2101.
4 K. Hiraki, R. Katayama, K. Yamaguchi and S. Honda, Inorg. Chim. Acta, 59 (1982) 11.
5 V. Alteparmakian, P. Mura, B.G. Olby and S.D. Robinson, Inorg. Chim. Acta, 104 (1985) L5.
6 B.E. Cavit, K.R. Grundy and W.R. Roper, J. Chem. Soc., Chem. Commun., (1972) 60.
7 A. Romero, A. Vegas, A. Santos and A.M. Cuadro, J. Chem. Soc., Dalton Trans., in press.
8 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
9 F.G. Moers and J.P. Langhout, Rec. Trav. Chim. Pays-Bas, 91 (1972) 591.
10 J.M. Jenkins and B.L. Shaw, J. Chem. Soc. (A), 770 (1966) 1407.
11 A. Romero, A. Vegas and A. Santos, J. Organomet. Chem., 310 (1986) C8.
12 G. van Koten and K. Vrieze, Adv. Organomet. Chem., 21 (1982) 151.
13 N. Ahmed, J.J. Levison, S.D. Robinson and M.F. Uttley, Inorg. Synth., 15 (1974) 48.
14 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1974.
15 J.M. Stewart, F.A. Kundell and J.C. Baldwin, X-ray'70 System, Computer Science Center, University of Maryland, College Park, Maryland, 1970.
16 C.K. Johnson, 1965. ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Tennessee.