RHODIUM(I) COMPLEXES WITH PYRIDAZINE, 4,6-DIMETHYL-PYRIMIDINE, 4,6-BIS(3,5-DIMETHYLPYRAZOL-1-YL)PYRIMIDINE, 3,6-BIS(3,5-DIMETHYLPYRAZOL-1-YL)PYRIDAZINE AND 3-(3,5-DIMETHYLPYRAZOL-1-YL)-6-CHLOROPYRIDAZINE

R. USON, L. A. ORO,* M. ESTEBAN and D. CARMONA Departamento de Química Inorgánica, Universidad de Zaragoza, Zaragoza, Spain

and

R. M. CLARAMUNT and J. ELGUERO*

Instituto de Química Médica, Juan de la Cierva 3, Madrid-6, Spain

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Abstract—The synthesis and properties of rhodium(I) complexes of formulae $[{RhCl(diolefin)}_2(L)]$ (or [RhCl(diolefin)(L)]), and $[Rh(diolefin)(L)]_n(ClO_4)_n$ are reported. These complexes react with carbon monoxide to yield the related carbonyl derivatives. Ligands used were pyridazine, 4,6-dimethyl-pyrimidine, 4,6-bis(3,5-dimethylpyrazol-1-yl)pyrimidine, 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine and 3-(3,5-dimethyl-pyrazol-1-yl)-6-chloropyridazine. Related iridium(I) and gold(I) compounds are also reported.

In recent years we have reported several types of polynuclear rhodium(I) complexes using ligands containing two or more nitrogen atoms, which are potentially capable of coordination to the metal ion.¹⁻⁴ In this paper we report some mono- or polynuclear rhodium(I) complexes with pyridazine (L^1) , 4,6-dimethyl-pyrimidine (L^2) , 4-6-bis(3,5-dimethylpyrazol-1-yl)pyrimidine (L^3) , 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine (L^4) , 3-(3,5-dimethylpyrazol-1-yl)pyridazine (L^5) and 3-(3,5-dimethylpyrazol-1-yl)pyridazine (L^6) , as well as some iridium(I) or gold(I) related complexes.

RESULTS AND DISCUSSION

Complexes with pyridazine (L^1) and 4,6dimethyl-pyrimidine (L^2)

The reaction of the pyridazine ligand (L^1) with binuclear rhodium(I) complexes of the type [RhCl(diolefin)]₂ (diolefin = tetrafluorobenzobarrelene, TFB,⁵ 2,5-norbornadiene, NBD⁶ or 1,5-cyclooctadine, COD⁷) (Rh/L¹ = 2 or 1) yielded mononuclear [RhCl(diolefin)(L¹)] complexes.⁸ In these reactions the pyridazine ligand behaved like pyridine.⁹ However, the 4,6-dimethyl-pyrimidine ligand (L²) reacted with $[RhCl(diolefin)]_2$ complexes (Rh/L² = 2 or 1) with formation of binuclear complexes of formula $[{RhCl(diolefin)}_2(L^2)]$ (diolefin = TFB or NBD), although molecular weight measurements (see Table 1) suggested a significant dissociation of the $[{RhCl(di$ $olefin)}_2(L^2)]$ complexes in chloroform solution.

Cationic complexes of formulae [Rh(diolefin) (L)]_n(ClO₄)_n (L = L¹ or L²) were formed by reaction of [Rh(diolefin)(Me₂CO)_x]ClO₄^{10,11} with the corresponding L¹ or L² ligand. In these compounds the two nitrogen atoms should be involved in bonding, but the products were generally too insoluble to establish the nuclearity.¹² The derived [Rh(CO)₂(L²)]_n(ClO₄)_n complex was obtained by bubbling carbon monoxide through a dichloromethane solution of [Rh(TFB)(L²)]_n(ClO₄)_n (Table 2).

Complexes with 4,6-bis(3,5-dimethylpyrazol-1-yl) pyrimidine(L^3), 3,5-bis(3,5-dimethylpyrazol-1-yl) pyridazine(L^4) and 3-(3,5-dimethylpyrazol-1-yl)-6-chloropyridazine(L^5)

While the binuclear cationic complex $[{Rh(COD)}_2(L^3)](ClO_4)_2$ was obtained by reaction of $[Rh(COD)(Me_2CO)_x]ClO_4$ with 4,6-bis(3,5-

^{*}Authors to whom correspondence should be addressed.

Complex	Analysis(found(ca	1cd)(\$))	Mol.wt.(CHC1,)	Yield	I.R. bands	
·	C	Н	N	(found(calcd.))	(1)	(cm ⁻¹)	
[RhC1(TFB)(L ¹)](I)	42.91 (43.22)	2.26 (2.27)	6.17 (6.30)	462 (445)	83	1570 ν(CN) 285 ν(RhCl)	
[RhC1(NBD)(L [†])](II)	42.99 (42.54)	3.78 (3.89)	8.72 (9.02)	329 (311)	66	1570,1575sh ν(CN) 270 ν(RhCl)	
[RhC1(COD)(L ¹)] (III)	44.08 (44.13)	4.88 (4.94)	8.48 (8.58)	312 (327)	73	1570 ν(CN) 280 ν(RhCl)	
[IrC1(COD)(L ¹)] (IV)	34.2 [.] 6 (34.65)	3.82 (3.88)	6.40 (6.73)		60	1565 ν(CN) 300 ν(IrC1)	
$[{RhC1(TFB)}_{2}(L^{2})](V)$	43.26 (43.03)	2.44 (2.40)	3.51 (3.34)	519 (837)	71	1610 ν(CN) 270 ν(RhCl)	
[{RhC1(NBD)};(L ²)](VI)	42.84 (42.21)	4.42	4.68 (4.92)	373 (569)	76	1610 ν(CN) 270 ν(RhCl)	

Table 1. Analytical results and properties for neutral complexes with L¹ and L² ligands

Table 2. Analytical results and properties for cationic complexes with L^1 and L^2 ligands

H .95 .98)	N 5.40 (5.51)	Orange	(1)	(cm ⁻¹)
.95 .98)	5.40	Orange	67	
	(3.31)		07	1580 V(CN)
.88 .23)	7.12 (7.48)	red	65	1575 ν(CN)
.78 .56)	6.43 (6.67)	red	8-3	1580 ∨(CN) 1710 ∨(CO)
.70 .63)	5.11 (5.22)	yellow	76	1625 V(CN)
.20 .20)	6.70 (7.64)	pale yellow	70	2110,2050 v(CO)
	.88 .23) .78 .56) .63) .20 .20)	.88 7.12 .23) (7.48) .78 6.43 .56) (6.67) .70 5.11 .63) (5.22) .20 6.70 .20) (7.64)	.88 7.12 red .23) (7.48) red .78 6.43 red .56) (6.67) red .63) (5.22) yellow .20 6.70 pale yellow	.88 7.12 red 65 .23) (7.48) red 83 .78 6.43 red 83 .56) (6.67) red 76 .63) (5.22) 76 76 .20 6.70 pale yellow 70 .20) (7.64) 76 70

dimethylpyrazol-1-yl)pyrimidine (L^3) $(Rh/L^3 =$ 2/1) (see Fig. 1a), mononuclear [Rh(diolefin) (L^4)]ClO₄ complexes (see Fig. 1b) were obtained by reaction of [Rh(diolefin)(Me₂CO)_x]ClO₄ with 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine (L⁴) $(Rh/L^4 = 2 \text{ or } 1/1)$. The related [Rh(diolefin)] (L^5)]ClO₄ complexes (see Fig. 1c) were similarly prepared. Furthermore, the tetrafluorobenzobarrelene mononuclear complexes [Rh(TFB) (L)]ClO₄ (L = L⁴ or L⁵) react with triphenylphosphine $(Rh/PPh_3 = 1/1)$ with formation of the presumed five-coordinated [Rh(TFB)(L) (PPh₃)]ClO₄ complexes.¹⁴

On the other hand, the reaction of $[Au(PPh_3)(Me_2CO)_x]ClO_4$ with L^4 $(Au/L^4 = 4/1)$ or L^5 $(Au/L^5 = 3/1)$ gave the trinuclear gold(I) complexes of formula $[{Au(PPh_3)}_3(L)](ClO_4)_3$, where all the nitrogen was involved in coordination with gold for L = L,⁵ but only three nitrogen atoms of

the four potentially capable of coordination, were used for L = L.⁴

Attempts to prepare an heterobinuclear rhodium(I)-gold(I)complex, by reaction of $[Rh(TFB)(L^4)]ClO_4$ with $[Au(PPh_3)(Me_2CO)_x]ClO_4$ in acetone as solvent were unsuccessful. The only isolated rhodium complex was [Rh(TFB)(L6)]ClO4 (see Fig. 1d) $(L^6 = 3-(3,5-dimethylpyrazol-1-yl)$ pyridazine). The formulation of the complex was confirmed by preparing the L⁶ ligand and subsequent reaction with [Rh(TFB)(Me₂CO)_x]ClO₄. The formation of [Rh(TFB)(L⁶)]ClO₄ from $[Rh(TFB)(L^4)]ClO_4$ corresponded to the hydrogenolysis of the $C_6 - N_{1''}$ bond between the pyridazine and the pyrazole. The N-unsubstituted 3,5-dimethylpyrazole has not been isolated; probably it forms gold complexes. A potential source of hydrogen could be the acetone used as solvent.

Bubbling carbon monoxide at atmospheric pres-



Fig. 1.

sure through dichloromethane solutions of the [Rh(diolefin)(L)]ClO₄ complexes (L = L⁴ or L⁵) gave rise to the formation of [Rh(CO)₂(L)]ClO₄ derivatives. In particular the [Rh(CO)₂(L⁵)]ClO₄ was also obtained by reacting [Rh(CO)₂ (Me₂CO)_x]ClO₄¹⁰ with L⁵. Furthermore, these dicarbonyl [Rh(CO)₂(L)]ClO₄ complexes reacted with triphenylphosphine with formation of the corresponding mononuclear [Rh(CO)(L)(PPh₃)] ClO₄ derivatives (see Scheme 1 and Table 3).

Binuclear neutral rhodium complexes of formula $[{RhCl(diolefin)}_2(L)]$ (L = L⁴, L⁵ or L⁶) were obtained by reacting $[RhCl(diolefin)]_2$ with L(Rh/L = 2/1). The rhodium atoms should be in a square planar arrangement where the L⁴, L⁵ or L⁶ ligands act as bridge between two "RhCl(diolefin)" units. Molecular weight measurements for L⁴ complexes suggest the existence, in some cases, of dissociation in chloroform solutions (Table 4).

The ¹H NMR measurements on these neutral complexes showed that only the 4-H and 5-H protons (see Fig. 1 for numbering scheme) were significantly broadened and shifted to lower field (ca. 0.6 ppm) by the coordination to the rhodium atom. The ¹³C NMR spectra of neutral complexes $[{RhCl(COD)}_{2}(L)], (L = L^{4}, L^{5} \text{ or } L^{6}) \text{ were also}$ recorded. Some of the quaternary carbons were not observed (marked with an asterisk in Fig. 2). The values in parentheses correspond to the $\Delta\delta$ differences in ppm between the chemical shifts of the free ligands (Table 6) and those of the complexes. The olefinic carbons of 1,5-cyclooctadiene appear at 80.1-80.5 ppm and are coupled with rhodium $({}^{1}J = 13 \text{ Hz})$; the saturated carbons appear at 30.8 ppm. No conclusion concerning the type of nitrogen atom involved in coordination, could be reached from these measurements.

The related [{RhCl(CO)₂}₂(L)] complexes were



Fig. 2.

Table 3. Analytical results and properties for cationic complexes with L^3 , L^4 , L^5 and L^6 ligands

Complex	Analysis	(found(a	alcd) (1))	Celour	$\Lambda_{\rm M}(\rm ohm^{-1})$ cm ² mo1 ⁻¹)	Yield (\$)	I.R. bands (cm ⁻¹)
$[{Rh(COD)}_{2}(L^{3})](Clo_{4})_{2}(XII)$	40.84 (40.51)	4.53 (4.53)	9.30 (9.45)	orange	180	89	1615,1580v(CN)
[Rh(TFB)(L ⁴)]C10 ₄ (XIII)	44.88 (44.81)	3.30 (3.18)	11.99 (12.06)	orange	128	86	1586,1560v(CN)
$[Rh(NBD)(L^4)]Clo_4$ (XIV)	44.16 (44.82)	4.16 (4.30)	14.90 (14.93)	orange	138	81 -	1565,1540v(CN)
$[Rh(COD)(L^4)]C10_4$ (XV)	44.82 (45.64)	5.16 (4.87)	13.89 (14.51)	pink	131	79	1580,1550v(CN)
[Rh(TFB)(L ⁵)]C10 ₄ (XVI)	38.76 (39.58)	2.81 (2.37)	8.21 (8.79)	orange		88	1575,1540v(CN)
[Rh(NBD)(L ⁵)]ClO ₄ (XVII)	37.29 (38.19)	3.38 (3.40)	10.78 (11.13)	orange	146	80	
[Rh(COD)(L ⁵)]C10 ₄ (XVIII)	38.46 (39.33)	3.96 (4.07)	11.02 (10.79)	pink	147	88.5	1575 ν(CN)
[Rh(TFB)(L ⁴)(PPh ₃)]C10 ₄ (XIX)	54.60 (55.10)	4.20 (3.89)	8.43 (8.76)	pale yellow		91	1585,1575, 1550 v(CN)
[Rh(TFB)(L ⁵)(PPh ₃)]Cl0 ₄ (XX)	51.44 (52.08)	3.35 (3.36)	5.80 (6.23)	yellow	140	92	1580,1540v(CN)
[Ir(CO)(L ⁴)(PPh ₃) ₂]ClO ₄ (XXI)	54.23 (55.06)	4.74 (4.17)	7.33 (7.55)	red brown		77	1935 v(CO) 1580,1550v(CN)
[Ir(CO)(L ⁵)(PPh ₃) ₂]ClO ₄ (XXII)	50.68 (52.47)	3.73 (4.85)	5.32 (5.84)	pale orang	8	69	1910 v(CO)
$[{Au(PPh_3)}_3(L^4)](Clo_4)_3$ (XXIII) 41.53 (42.00)	3.73 (3.16)	4.81 (4.32)	white	298	46	1575,1560v(CN)
$[{Au(PPh_3)}_3(L^5)](C10_4)_3$ (XXIV)	40.07 (40.15)	2.95 (2.88)	3.48 (2.97)	white	267	70	1560 ν(CN)
[Rh(TFB)(L ⁶)]Cl0 ₄ (XXV)	42.55 (41.85)	2.93 (2.67)	8.82 (9.29)	orange	113	73	1595 v(CN)
[Rh(CO) ₂ (L ⁴)]ClO ₄ (XXVI)	36.90 (36.49)	3.36 (3.06)	15.63 (15.95)	orange		92	2105,2050v(Ci
[Rh(CO) ₂ (L ⁵)]ClO ₄ (XXVII)	27.75 (28.29)	1.80 (1.94)	11.57 (11.99)	violet	•••	75	2100,2060v(C
[Rh(CO)(L ⁴)(PPh ₃]]C10 ₄ (XXVIII)	50.68 (52.09)	4.35 (4.11)	10.85 (11.04)	pale orang	è	89	1945 v(CO)
[Rh(CO)(L ⁵)(PPh ₃)]C10 ₄ (XXIX)	48.20 (47.95)	3.68 (3.45)	7.87 (7.99)	orange	144	76	1995 v(CO)

prepared by carbonylation of the corresponding diolefinic parent complexes, or by reaction of $[RhCl(CO)_2]_2^{15}$ with L (see Scheme 1). However, an alternative formulation for these complexes is $[Rh(CO)_2(L)][RhCl_2(CO)_2]$, supported by the presence of four $\nu(CO)$ bands in the range 1985–2110 cm⁻¹, but the insolubility of these materials prevents us from conductivity measurements.

EXPERIMENTAL

Melting points are uncorrected and were mea-

sured on a Büchi–Tottoli instrument. The C, H and N analyses were carried out with a Perkin–Elmer 240B microanalyzer. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer. ¹H NMR and ¹³C NMR were obtained with a Bruker WP 80SY spectrometer using CDCl₃ solvent. Chemical shifts are given in ppm (δ scale) relative to internal TMS. Molecular weights were determined osmometrically with a Perkin–Elmer 115 instrument. Conductivities were measured in 5×10^{-4} M acetone solution with a

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Complex		•	nalysi:		Mol.wt.(CHCl ₃)	Colour	Yield	I.R. bands
		(found C	l(calcd. H	((1))	(found(calcd))		Ξ	(cm])
[{RhC1(TFB)} ₂ (L ⁴)]	(xxx)	45.84 (45.76)	2.89 (2.83)	8.33 (8.43)	1168 (998)	orange	8	1575,1545 v(CN) 298 v(RhCl)
[{RhC1(NBD)} ₂ (L ⁴)]	(IXXI)	45.42 (46.11)	4.43 (4.42)	11.62 (11.52)	623 (729)	orange	78	1587,1571,1550 v(CN) 259 v(RhCl)
[{RhC1(COD)} ₂ (L ⁴)]	(XXXII)	46.95 (47.32)	5.25 (5.29)	11.24 (11.04)	419 (761)	yellow	88	1575,1550 v(CN) 250 v(RhCl)
[{RhC1(TFB)} ₂ (L ⁵)]	(IIIXXX)	41.64 (42.27)	2.35 (2.26)	5.44 (5.97)		red-brown	63	1580,1565 v(CN) 290 v(RhCl)
[{khc1(NBD)} ₂ (L ⁵)]	(XXXIV)	40.45 (41.25)	3.76 (3.85)	$^{8.37}_{(7.76)}$		red-brown	73	1580,1540 v(CN) 265 v(RhCl)
[{khc1(cod)} ₂ (L ⁵)]	(XXXV)	41.66 (42.79)	4.33 (4.74)	8.24 (7.98)		pink	85	1580,1540 v(CN) 270 v(RhCl)
[{RhC1(C0) ₂ } ₂ (L ⁴)]	(XXXVI)	32.65 (32.90)	2.36 (2.45)	12.65 (12.79)		dark-blue	85	2110,2070,2045,1985 v(CO) 320,290 v(RhCl)
[{khc1(c0) ₂ } ₂ (L ⁵)]	(XXXVII)	25.95 (26.13)	1.54 (1.52)	9.83 (9.38)		blue	78	2100,2060,2030,1990 v(CO) 320,290 v(RhCl)
[{syc1(cod)} ² (L ⁶)]	(111/XXX)	44.78 (45.00)	4.98 (5.13)	8.30 (8.40)		orange	81	1580,1540 v(CN) 250 v(RhCl)

Table 4. Analytical results and properties for neutral complexes with L^4 , L^5 and L^6 ligands



Scheme 1. $L = L^4$ or L^5 .

Ligand ^{a,e}	2-H	4 - H	5-H	6-H	4'-H	3'-CH ₃	5'-CH3
L ^{3 b}	8.72	-	8.37	-	6.00	2.28	2.70
l ⁴	-	8.19	8.19	-	6.02	2.27	2.72
L ⁵ c	-	8.23	7.66	-	6.13	2.32	2.77
L ^{6 d}	-	8.09	7.45	9.00	6.00	2.27	2.73

Table 5. ¹H NMR data for L³, L⁴, L⁵ and L⁶ ligands

J(4-H,6-H)= 1.54 Hz, J(5-H,6-H)= 4.8 Hz. ^eSolvent was CDC1₃.

a For nu	mbering	scheme.	see F	ig 1.	^b J(1-H,C	$H_{z}) = 0.83$	Hz,
L ^{6 d}	-	8.09	7.45	9.00	6.00	2.27	2.73
L ^{5 c}	-	8.23	7.66	-	6.13	2.32	2.77
-							

Table 6. ¹³C NMR data for L³, L⁴, L⁵ and L⁶ ligands

Ligan	l ^{a,b} 2-C	3-C	4-C	5-C	6-C	3'-C	4'-C	5'-C	3'-CH ₃	5'-CH ₃
L ³	156.8		160.3	98.5		151.2	110.7	142.7	13.6	15.2
l ⁴		155.0	122.7	-		151.1	110.0	142.2	13.6	14.7
l ⁵		156.0	122.4	130.0	153.4	151.6	110.6	142.5	13.5	14.9
L ⁶		156.6	120.0	129.3	150.0	150.4	110.0	141.5	13.4	14.4

^aFor numbering scheme see Fig 1. ^bSolvent were: CDC1₃ (for L^4 and L^5), DMSO-d₆ (for L^6) and $CDC1_3 + DMSO - d_6$ (for L^3).

Philips 9501/01 conductimeter. Direct inlet MS were registered on a Hitachi Perkin-Elmer RMU-6M spectrometer.

Synthesis of ligands

The synthesis of 3,6-bis(3,5-dimethylpyrazol-1yl)pyridazine (L⁴) and 3-(3,5-dimethylpyrazol-1yl)-6-chloro-pyridazine (L⁵) have been previously reported.¹⁶

Synthesis of 4,6-bis(3,5-dimethylpyrazol-1-yl)pyrimidine (L^3)

To a solution of 4,8 g (0.05 mol) of 3.5-dimethylpyrazole in 250 cm³ of anhydrous xylene, 1.2 g (0.052 mol) of finely divided sodium metal were added. The reaction mixture was stirred overnight at room temperature. Then 3.72 g (0.025 mol) of 4,6-dichloropyrimidine in anhydrous xylene were added with a dropping funnel to the suspension of 3,5-dimethylpyrazole sodium salt. After heating under reflux for 12 hr, the solution was filtered and the filtrate evaporated under vacuum. The resulting solid was crude 4,6-bis(3,5-dimethylpyrazol-1-yl)pyrimidine (Yield: 93%), which was purified by column chromatography on silica-gel (60 Merck) using chloroform as eluent. M.p., 148°C. Mass spectrum: m/e268 (M⁺).

Synthesis of 3-(3,5-dimethylpyrazol-1-yl)pyridazine (L^6)

A mixture of 0.6 g (0.003 mol) of 3-(3,5dimethylpyrazol-1-yl)-6-chloropyridazine, 5 cm3 of aqueous NH₄OH (25%) 70 cm³ of methanol and

0.5 g of Pd/C (10%) was catalytically hydrogenated at an initial pressure of 35 psi. After 20 min, the reaction was ceased and worked up, filtered, washed with chloroform (100 cm³) and evaporated *in vacuo*. The low melting solid (m.p., 40°C) obtained was 3-(3,5-dimethylpyrazol-1-yl)pyridazine. Mass spectrum: m/e 174 (M⁺).

When the reaction time was longer the pyridazine ring was hydrogenated too. Thus after 6 hr the tetrahydropyridazine was formed (m.p.: 88–90°C); mass spectrum (m/e 178(M⁺)) and proton magnetic resonance confirming the assigned structure: ¹H NMR (CDCl₃) δ : 1.8–3.3(m, 6H), 2.27(s,3H), 2.44(s,3H), 5.47(br,NH) and 5.94(s, pyrazolic proton).

¹H NMR and ¹³C NMR for L^3 , L^4 , L^5 and L^6 ligands are listed in Tables 5 and 6.

Preparation of complexes of the type $[RhCl(diolefin)(L^1)]$

The preparation of $[RhCl(TFB)(L^1)]$ is described as an example.

Addition of $13 \ \mu l$ (0.179 mmol) of L¹ to a suspension of 58.9 mg (0.08 mmol) of [RhCl(TFB)]₂⁵ in 5 cm³ of acetone caused immediate dissolution of the solid. The resulting yellow solution was stirred for 20 min and *vacuum*-concentrated to *ca*. 2 cm³. Slow addition of hexane caused precipitation of a yellow solid, which was filtered off, washed with hexane and air-dried.

Preparation of complexes of the type $[{RhCl(diolefin)}_{2}(L^{2})]$

The preparation of $[{RhCl(NBD)}_2(L^2)]$ is described as an example.

To a suspension of 101.8 mg (0.220 mmol) of $[RhCl(NBD)]_2^6$ in 5 cm³ of acetone were added 27 μ l (0.245 mmol) of L², which caused immediate dissolution of the initial complex and formation of a yellow solid. After 20 min stirring, the suspension was *vacuum*-concentrated to half its volume and the precipitation was completed by addition of hexane. The yellow solid was filtered off, washed with hexane and air-dried.

Preparation of [IrCl(COD)(L¹)]

Addition of 11 μ l (0.151 mmol) of the ligand to a suspension of 40.4 mg (0.061 mmol) of [IrCl-(COD)]₂¹⁷ in 5 cm³ of acetone gives an orange solution. After stirring, under nitrogen, this solution for 15 min, was *vacuum*-concentrated to *ca*. 1 cm³ and a lemon-yellow solid appeared, which was filtered off and air-dried. Preparation of complexes of the type $[Rh(diolefin)(L)]_n(ClO_4)_n$ $(L = L^1, L^2)$

The preparation of $[Rh(TFB)(L^1)]_n(ClO_4)_n$ is described as an example.

To a suspension of 50.8 mg (0.070 mmol) of $[RhCl(TFB)]_2$ in 5 cm³ of acetone was added silver perchlorate (31.5 mg, 0.152 mmol) in 2 cm³ of the same solvent. Silver chloride was immediately precipitated. After 30 min stirring the silver chloride was filtered off and 11 μ l (0.151 mmol) of L¹ were added to the filtrate. The colour changes from yellow to orange and an orange solid appeared. After 20 min stirring, the suspension was concentrated to half its volume and addition of hexane completed the precipitation of the complex, which was filtered off, washed with hexane and air-dried.

Preparation of $[Rh(CO)_2(L^2)]_n(ClO_4)_n$

Carbon monoxide at normal pressure was bubbled through a suspension of [Rh(TFB) $(L^2)]_n(CIO_4)_n$ in dichloromethane, for 45 min, during which a pale yellow solid precipitated. This solid was filtered off, washed with ether and airdried.

Preparation of $[{Rh(COD)}_2(L^3)](ClO_4)_2$

Addition of 69.1 mg (0.333 mmol) of silver perchlorate in 2 cm³ of acetone to a suspension of 76.2 mg (0.154 mmol) of $[RhCl(COD)]_2^7$ in 10 cm³ of the same solvent gave an immediate precipitation of silver chloride. The suspension was stirred for 30 min, the precipitate was filtered off, and the filtrate was added to a solution of 42.5 mg (0.158 mmol) of the ligand in 10 cm³ of acetone. The resulting orange solution was stirred for 15 min and *vacuum*-concentrated to *ca.* 2 cm³, whereupon an orange solid separated. The precipitation was completed by adding ether, and the solid was filtered off, washed with ether and airdried.

Preparation of complexes of the type $[Rh(diolefin)(L)]ClO_4$ $(L = L^4, L^5)$

The preparation of $[Rh(COD)(L^5)]ClO_4$ was described as an example.¹⁸

To a suspension of 50.9 mg (0.103 mmol) of $[RhCl(COD)]_2$ in 10 cm^3 of acetone was added silver perchlorate (43.9 mg; 0.212 mmol) in 2 cm³ of the same solvent. After 45 min stirring the formed silver chloride was filtered off and the filtrate was added to 43.1 mg (0.206 mmol) of the ligand in 10 cm^3 of acetone. The colour changed from yellow to red. This solution was stirred for 20 min and *vacuum*-concentrated to *ca*. 1 cm³ and slow addition of ether gave a precipitate of a pink solid, which was filtered off, washed with ether and air-dried.

Preparation of complexes of the type $[Rh(TFB)(L)(PPh_3)]ClO_4$ (L = L⁴, L⁵)

The preparation of $[Rh(TFB)(L^4)(PPh_3)]ClO_4$ is described as an example.

A stoichiometric amount of triphenylphosphine in dichloromethane was added to a solution of $[Rh(TFB)(L^4)]ClO_4$ in 10 cm³ of the same solvent. The colour changed from orange to orange-yellow. After 25 min stirring, the solution was *vacuum*-concentrated to *ca.* 1 cm³ and slow addition of ether gave a yellow solid, which was filtered off, washed with ether and air-dried.

Reaction between $[Rh(TFB)(L^4)]ClO_4$ and $[Au(PPh_3)(Me_2CO)_x]ClO_4$

To a solution of 21.8 mg (0.044 mmol) of AuCl(PPh₃) in 10 cm³ of acetone were added 9.7 mg (0.047 mmol) of silver perchlorate in 2 cm³ of the same solvent. The silver chloride formed was filtered off after 25 min stirring and the filtrate was added to a suspension of 30.6 mg (0.044 mmol) of [Rh(TFB)(L⁴)]ClO₄ in 5 cm³ of acetone. The resulting orange solution was stirred for 20 min and *vacuum*-concentrated to *ca*. 2 cm³; the precipitation of the orange complex was completed by slow addition of ether. The solid was filtered off, washed with ether, air-dried and identified as [Rh(TFB)(L⁴)]ClO₄.

Preparation of complexes of the type $[Rh(CO)_2(L)]ClO_4$ (L = L⁴, L⁵)

These complexes were made by the two routes described below.

(i) Preparation of $[Rh(CO)_2(L^4)]ClO_4$. Carbon monoxide at normal pressure was bubbled for 30 min through a dichloromethane solution of 39.8 mg (0.07 mmol) of $[Rh(NBD)(L^4)]ClO_4$. The colour changed from orange to yellow. This solution was *vacuum*-concentrated and slow addition of ether completed the precipitation of a yellow solid, which was filtered off, washed with ether and air-dried.

(ii) Preparation of $[Rh(CO)_2(L^5)]ClO_4$. Addition of 36.9 mg (0.178 mmol) of silver perchlorate in 2 cm³ of acetone to a solution of 33.4 mg (0.086 mmol) of $[RhCl(CO)_2]_2^{15}$ in 10 cm³ of acetone gave an immediate precipitate of silver chloride. After 30 min stirring, the silver chloride was filtered off and the filtrate was added to 36.3 mg (0.173 mmol) of L⁵ in 5 cm³ of acetone. The resulting green suspension was stirred for 20 min and *vacuum*-concentrated to half its volume. The precipitation was completed by adding ether and the resulting violet solid was filtered off, washed with ether and air-dried. Preparation of complexes of the type $[Rh(CO)(L)(PPh_3)]ClO_4$ (L = L⁴, L⁵)

These two complexes were prepared by the method described below.

Carbon monoxide was bubbled for 60 min through a solution of $[Rh(TFB)(L)]ClO_4$ ($L = L^4$, L^5) and a stoichiometric amount of triphenylphosphine in dichloromethane was added. The resulting orange solution was *vacuum*concentrated to *ca.* 1 cm³ and slow addition of ether completed the precipitation of an orange solid, which was filtered off, washed with ether and air-dried.

Preparation of complexes of the type $[{Au(PPh_3)}_3(L)](ClO_4)_3 (L = L^4, L^5)$

The preparation of $[{Au(PPh_3)}_3(L^4)](ClO_4)_3$ is described as an example.

To a suspension of 99.7 mg (0.201 mmol) of AuCl(PPh₃)¹⁹ in 10 cm³ of acetone were added 43.8 mg (0.211 mmol) of silver perchlorate in 2 cm³ of the same solvent. After 20 min stirring, under nitrogen, the silver chloride was filtered off and the filtrate was added to a solution of 13.5 mg (0.05 mmol) of L⁴. The resulting colorless solution was stirred for 20 min. Slow addition of ether to a *vacuum*-concentrated solution gave a white solid, which was filtered off, washed with ether and air-dried. The complex was recrystallised from dichloromethane/ether.

Preparation of complexes of the type $[Ir(CO)(L)(PPh_3)_2]CIO_4$ (L = L⁴, L⁵)

The synthesis of $[Ir(CO)(L^4)(PPh_3)_2]ClO_4$ is described as an example.

A suspension of 59.5 mg (0.076 mmol) of *trans*-IrCl(CO)(PPh₃)₂²⁰ in 10 cm³ of acetone was stirred, under nitrogen, for 30 min together with 17.4 mg (0.084 mmol) of silver perchlorate. The resulting silver chloride was filtered off and the filtrate was added to a solution of 20.6 mg (0.077 mmol) of L⁴ in 10 cm³ of acetone. The colour changed from yellow to orange. After 15 min stirring, the orange solution was *vacuum*-concentrated to *ca*. 2 cm³. Addition of ether completed the precipitation of a red-brown solid which was filtered off, washed with ether and air-dried.

Preparation of complexes of the type $[{RhCl(diolefin)}_{2}(L)]$ (L = L⁴, L⁵, L⁶)

These complexes were prepared as is described below for $[{RhCl(COD)}_2(L^4)]$.

To a suspension of 50.3 mg (0.102 mmol) of $[RhCl(COD)]_2$ in 10 cm^3 of acetone were added 27.7 mg (0.103 mmol) of L⁴. The colour changed from yellow to orange. The suspension was stirred

for 20 min and *vacuum*-concentrated to $ca. 2 \text{ cm}^3$. Addition of ether completed the precipitation of the complex, which was filtered off, washed with ether and air-dried.

Preparation of complexes of the type $[{RhCl(CO)_2}_2(L)]$ $(L = L^4, L^5)$

These complexes were prepared by the two routes described below.

(i) Carbon monoxide at normal pressure was bubbled through a solution of $[{RhCl(COD)}_2(L)]$ $(L = L^4 \text{ or } L^5)$ in dichloromethane for 30 min, which caused the precipitation of the carbonylated complex which was filtered off, washed with ether and air-dried.

(ii) 17.6 mg (0.084 mmol) of L^5 were added to a solution of $[RhCl(CO)_2]_2$ (32 mg, 0.082mmol) in dichloromethane. A green solid precipitated immediately. The suspension was stirred for 30 min and concentrated to *ca*. 2 cm³. Slow addition of ether completed the precipitation of the solid, which was filtered off, washed with ether and air-dried.

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