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RHODIUM(I) INDAZOLE AND INDAZOLATE COMPLEXES

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Summary

The preparation of cationic indazole (HIdz) rhodium(I) complexes of the types $[(\text{diolefin})Rh(HIdz)_2]ClO_4$ and $[(CO)_2Rh(HIdz)_2]ClO_4$ is described. Neutral binuclear rhodium(I) complexes of the type $[Y_2Rh(\mu\text{-}Idz)]_2$ (Y_2 = COD, TFB, NBD, $(CO)_2$ or $(CO)(PPh_3)$) are obtained by treating the corresponding complexes $[Y_2RhCl]_2$ with indazole and organic or inorganic bases. The cationic mononuclear derivatives react with the solvated species $[Y_2Rh(\text{acetone})_x]ClO_4$ in the presence of triethylamine to give neutral binuclear complexes of the types $[(CO)_2Rh(\mu\text{-}Idz)_2Rh(\text{diolefin})]$, $[(Ph_3P)(CO)Rh(\mu\text{-}Idz)_2Rh(\text{diolefin})]$ and $[(\text{diolefin})Rh(\mu\text{-}Idz)Rh(\text{diolefin}')]$ (diolefin = COD, TFB or NBD; diolefin' = COD or TFB). Alternative methods for the synthesis of the binuclear complexes are also described.

Introduction

Pyrazolate can act as an exobidentate bridging ligand between two metal centres [1–6]. This may lead to cooperative catalytical or electrical effects between the adjacent metals [7]. Nevertheless, neutral indazole as ligand in rhodium chemistry has been little studied [8,9].

Indazole is a weak base (p*K*a = 1.31 [10]) and also a weak acid able to produce the indazolate (Idz) ion in basic medium. We describe here a family of cationic and neutral rhodium(I) complexes containing the 2-monohaptoindazole and 1,2-dihaptoindazolate ligands.

Results and discussion

Cationic complexes

Addition of indazole to dichloromethane solutions of compounds of the type $[Rh(\text{diolefin})_2]ClO_4$ causes rapid displacement of one of the diolefin groups, according to eq. 1.

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$$[\mathrm{Rh(diolefin)_2}]\mathrm{ClO_4} + 2\ \mathrm{HIdz} \rightarrow \underset{\text{(I–III)}}{[\mathrm{(diolefin)Rh(HIdz)_2}]\mathrm{ClO_4}} + \text{diolefin} \qquad (1)$$

(diolefin = 1,5-cyclooctadiene (COD) (I); tetrafluorobenzobarrelene (TFB) (II); 2,5-norbornadiene (NBD) (III)).

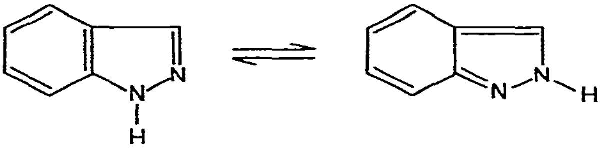
The resulting yellow microcrystalline solids (complexes I–III) behave as 1:1 electrolytes in acetone [11]. Their conductivities and analytical data are listed in Table 1. These complexes can also be prepared, but less pure, by the reaction of indazole with the solvated species $[\mathrm{(diolefin)Rh(Me_2CO)_x}]^+$ [12].

The acid hydrogen atom of the indazole ligand can be removed with ease, e.g. addition of potassium hydroxide to methanol solutions of $[\mathrm{(COD)Rh(HIdz)_2}]\mathrm{ClO_4}$ gives the binuclear complex $[\mathrm{(COD)Rh(\mu\text{-}Idz)}]_2$, which separates as yellow crystals, and addition of perchloric acid and indazole to the binuclear complex regenerates the cationic complex (eq. 2).

$$[\mathrm{(COD)Rh(HIdz)_2}]\mathrm{ClO_4} \xrightleftharpoons[\mathrm{HClO_4 + HIdz}]{\mathrm{KOH}} 1/2[\mathrm{(COD)Rh(\mu\text{-}Idz)}]_2 \qquad (2)$$

Bubbling of carbon monoxide through dichloromethane solutions of $[\mathrm{(COD)Rh(HIdz)_2}]\mathrm{ClO_4}$ leads to the displacement of the 1,5-cyclooctadiene and to the formation of the yellow microcrystalline compound $[\mathrm{(CO)_2Rh(HIdz)_2}]\mathrm{ClO_4}$ (IV), which behaves as a 1:1 electrolyte in acetone. The IR spectrum of the solid shows two bands due to ν(CO) at 2100 and 2035 $\mathrm{cm^{-1}}$, which are characteristic of a rhodium(I) *cis*-dicarbonyl [13]. Moreover, in dichloromethane solution four bands assignable to ν(CO) are observed at 2100vs, 2040vs and 2085s, 2015s $\mathrm{cm^{-1}}$ and point to the presence of two different *cis*-dicarbonyl species in solution. One of these species must be identical with the species present in the solid, because of the coincidence of the location of the corresponding bands. Furthermore, dichloromethane solutions of $[\mathrm{(CO)_2Rh(HPz)_2}]\mathrm{ClO_4}$ [14] (HPz = pyrazole), which show bands arising from ν(CO) at 2100vs, 2040vs and 2095s, 2015s $\mathrm{cm^{-1}}$ with the same pattern as in the indazole derivative IV, must also contain these two species. Therefore, the apparent splittings must be due to effects caused by the coordinated pyrazole group.

In addition, the ^{1}H NMR spectrum of complex IV (in deuterochloroform at room temperature) shows complex multiplets between δ 8.20 and 7.06 ppm, which are slightly displaced relative to the free ligand [15]. On the other hand, the free ligand exhibits a broad band with a maximum centred towards δ 11.1 ppm (in deuterochloroform) arising from the pyrolic proton of the tautomeric equilibrium [16]:



whilst complex IV shows two singlets at δ 12.4 and 12.0 ppm, which correspond to two pyrrolic protons in a chemically inequivalent environment. The spectroscopic data can be interpreted by assuming that there is exchange of the pyrrolic proton between the two nitrogen atoms in solution. Similar behaviour was suggested for pyrazole complexes of platinum, e.g. $\mathrm{PtI_2(HPz)_2}$ [17].

TABLE 1

ANALYTICAL AND OTHER DATA FOR CATIONIC Rh^I COMPLEXES

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)	ν(NH) (Nujol)(cm^{-1})
	C	H	N			
I [(COD)Rh(HIdz)$_2$]ClO$_4$	48.4 (48.3)	4.5 (4.4)	10.4 (10.3)	131	88	3270s(b)
II [(TFB)Rh(HIdz)$_2$]ClO$_4$	47.0 (47.0)	2.8 (2.7)	8.4 (8.4)	122	81	3600(b), 3450s, 3350s(b)
III [(NBD)Rh(HIdz)$_2$]ClO$_4$	47.6 (47.5)	3.8 (3.8)	10.6 (10.6)	135	87	3320(b), 3260(b)
IV [(CO)$_2$Rh(HIdz)$_2$]ClO$_4$	38.9 (38.8)	3.1 (2.4)	10.7 (11.3)	134	79	3330s(b) 3240s

TABLE 2

ANALYTICAL AND OTHER DATA FOR DINUCLEAR COMPLEXES OF THE TYPE [Y_2Rh(μ-Idz)]$_2$

Complex	Found (calcd.) (%)			Mol. weight	M.p. (°C)	Yield (%)	Colour	ν(CO) (CH_2Cl_2) (cm^{-1})
	C	H	N					
V [(COD)Rh(μ-Idz)]$_2$	54.7 (54.9)	5.2 (5.2)	8.4 (8.5)	712 (656)	270	90	orange	
VI [(TFB)Rh(μ-Idz)]$_2$	51.4 (51.1)	2.6 (2.5)	6.2 (6.3)	813 (892)	300	87	orange	
VII [(NBD)Rh(μ-Idz)]$_2$	53.8 (53.9)	4.2 (4.2)	9.1 (9.0)	587 (624)	273	86	red	
VIII [(CO)$_2$Rh(μ-Idz)]$_2$	39.3 (39.2)	1.8 (1.8)	10.4 (10.15)	605 (552)	131	88	yellow	2095, 2085, 2025
IX [(Ph_3P)(CO)Rh(μ-Idz)]$_2$	61.2 (61.2)	4.3 (3.95)	5.2 (5.5)	943 (1020)	202	77	yellow	1975,1960

Binuclear complexes of the type $[Y_2Rh(\mu\text{-}Idz)]_2$ *(*Y_2 *= diolefin,* $(CO)_2$ *or* $(PPh_3)(CO)$*).*
$[(COD)Rh(HIdz)_2]ClO_4$ reacts with potassium hydroxide, as mentioned above, or also with $[(COD)Rh(Me_2CO)_x]ClO_4$ in the presence of triethylamine to give the binuclear complex $[(COD)Rh(\mu\text{-}Idz)]_2$ (V). This type of compound can be obtained directly according to eq. 3.

$$[(\text{diolefin})Rh(\mu\text{-}Cl)]_2 + 2\ HIdz + 2\ NaOH \rightarrow [(\text{diolefin})Rh(\mu\text{-}Idz)]_2 + 2\ NaCl + 2\ H_2O$$

$$(\text{diolefin} = \text{COD (V); TFB (VI); NBD (VII)}) \tag{3}$$

The binuclear complexes are air-stable crystals. Their analytical data and molecular weights are listed in Table 2.

The acidity of the pyrrolic hydrogen atom of the indazole can coveniently be used for the synthesis of the binuclear complex $[(CO)_2Rh(\mu\text{-}Idz)]_2$ (VIII), according to the following reactions (eq. 4).

$$\left.\begin{array}{l}(CO)_2Rh(acac)\\ 1/2[(CO)_2Rh(\mu\text{-}Cl)]_2\end{array}\right] \xrightarrow[NEt_3]{HIdz} 1/2[(CO)_2Rh(\mu\text{-}Idz)]_2 \tag{4}$$

Bubbling of carbon monoxide through solutions of $[(COD)Rh(\mu\text{-}Idz)]_2$ and subsequent addition of triphenylphosphine gives rise to the formation of $[(Ph_3P)(CO)Rh(\mu\text{-}Idz)]_2$ (IX), which may also be obtained by treatment of $[(Ph_3P)(CO)Rh(\mu\text{-}Cl)]_2$ with indazole and sodium hydroxide.

Other binuclear complexes.
The tetracarbonyl $[(CO)_2Rh(\mu\text{-}Idz)]_2$ reacts with an excess of cyclooctadiene in refluxing dichloromethane to give $[(COD)Rh(\mu\text{-}Idz)]_2$, whilst bubbling of carbon monoxide through a solution of $[(COD)Rh(\mu\text{-}Idz)]_2$ causes the ready displacement of both cyclooctadiene groups and the formation of $[(CO)_2Rh(\mu\text{-}Idz)]_2$, the only species which could be detected in solution by IR spectroscopy. However, attempts to precipitate this species from the solutions which contain the displaced cyclooctadiene yield the complex $[(COD)Rh(\mu\text{-}Idz)_2Rh(CO)_2]$ (X). The equilibria involved are shown in eq. 5.

$$[(COD)Rh(\mu\text{-}Idz)]_2 \xrightleftharpoons[COD]{2CO} [(COD)Rh(\mu\text{-}Idz)_2Rh(CO)_2] \xrightleftharpoons[COD]{2CO} [(CO)_2Rh(\mu\text{-}Idz)]_2 \tag{5}$$

In accordance with this interpretation, complex X can also be obtained by treatment of the tetracarbonyl VIII with a stoichiometric amount of 1,5-cyclooctadiene in refluxing dichloromethane.

As in eq. 4, the acidity of the pyrrolic hydrogen atom of the coordinated indazole can be utilized in the preparation of this type of complex, according to the general process represented in eqs. 6 and 7.

$$[(\text{diolefin})Rh(HIdz)_2]ClO_4 + (acac)Rh(CO)_2 + NEt_3 \rightarrow [(\text{diolefin})Rh(\mu\text{-}Idz)_2Rh(CO)_2] + Hacac + (HNEt_3)ClO_4 \tag{6}$$

$$[(\text{diolefin})Rh(HIdz)_2]ClO_4 + [(Me_2CO)_xRh(CO)_2]ClO_4 + NEt_3 \rightarrow [(\text{diolefin})Rh(\mu\text{-}Idz)_2Rh(CO)_2] + xMe_2CO + 2(HNEt_3)ClO_4 \tag{7}$$

(diolefin = COD (X), TFB (XI), NBD (XII))

In both cases a small amount of the binuclear complexes $[(\text{diolefin})\text{Rh}(\mu\text{-Idz})]_2$ and $[(\text{CO})_2\text{Rh}(\mu\text{-Idz})]_2$ is also formed. Separation from the main products can be accomplished by making use of the differential solubilities.

The analytical data and molecular weights of complexes X–XII show them as binuclear (Table 3). Their IR spectra in solution exhibit bands due to $\nu(\text{CO})$, which are characteristic of *cis*-Rh^{I} dicarbonyls, as was observed for the complexes $[(\text{azobenzene})_2\text{Rh}^{\text{III}}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$ [18] and $[(\text{COD})\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$ [19].

The method represented by eq. 7 also enabled us to prepare mixed binuclear complexes of the type $[(\text{diolefin})\text{Rh}(\mu\text{-Idz})_2\text{Rh}(\text{diolefin}')]$ (eq. 8).

$$[(\text{diolefin})\text{Rh}(\text{HIdz})_2]\text{ClO}_4 + [(\text{Me}_2\text{CO})_x\text{Rh}(\text{diolefin}')]\text{ClO}_4 + 2\ \text{NEt}_3 \rightarrow$$
$$[(\text{diolefin})\text{Rh}(\mu\text{-Idz})_2\text{Rh}(\text{diolefin}')] + x\text{Me}_2\text{CO} + 2(\text{HNEt}_3)\text{ClO}_4 \quad (8)$$

diolefin	diolefin′	
COD	TFB	(XIII)
COD	NBD	(XIV)
TFB	NBD	(XV)

The analytical data and molecular weights of the resulting complexes XIII–XV are listed in Table 3. Their IR spectra exhibit bands which are characteristic of coordinated diolefins (TFB at 1500s, 1040s and 885s cm^{-1}; NBD at 1310m cm^{-1}; or COD at 1320 and 1300w cm^{-1}). Moreover, the ^{1}H NMR spectrum of complex XIII shows the diolefins COD and TFB in 1 : 1 molar ratio. Finally, X-ray diffraction studies (Debye-Scherrer) of complexes X and XIII do not coincide in the diffraction maxima, although because of its lower crystallinity the second shows much more diffuse scattering than the first.

A general method for the preparation of complexes of the type $[(\text{diolefin})\text{Rh}(\mu\text{-Idz})_2\text{Rh}(\text{CO})(\text{PPh}_3)]$ based on eqs. 6 and 7 can be summarized as follows (eqs. 9 and 10).

$$[(\text{diolefin})\text{Rh}(\text{HIdz})_2]\text{ClO}_4 + (\text{acac})\text{Rh}(\text{CO})(\text{PPh}_3) + \text{NEt}_3 \rightarrow$$
$$[(\text{diolefin})\text{Rh}(\mu\text{-Idz})_2\text{Rh}(\text{CO})(\text{PPh}_3)] + \text{Hacac} + (\text{HNEt}_3)\text{ClO}_4 \quad (9)$$
$$[(\text{diolefin})\text{Rh}(\text{HIdz})_2]\text{ClO}_4 + [(\text{Me}_2\text{CO})_x\text{Rh}(\text{CO})(\text{PPh}_3)]\text{ClO}_4 + 2\ \text{NEt}_3 \rightarrow$$
$$[(\text{diolefin})\text{Rh}(\mu\text{-Idz})_2\text{Rh}(\text{CO})(\text{PPh}_3)] + 2(\text{HNEt}_3)\text{ClO}_4 \quad (10)$$

(diolefin = COD (XVI); TFB (XVII); NBD (XVIII))

Complexes XVI–XVIII are yellow or orange microcrystalline solids. Their analytical data and molecular weights are listed in Table 3. Their IR spectra exhibit a single band due to $\nu(\text{CO})$ at ~ 1980 cm^{-1}, which is characteristic of mononuclear Rh^{I} complexes. Furthermore, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of XVI shows a doublet at $\delta = 24.7$ (d, $^1J(\text{Rh–P}) = 127$ Hz).

Bubbling carbon monoxide through dichloromethane solutions of XVI gives $[(\text{CO})_2\text{Rh}(\mu\text{-Idz})_2\text{Rh}(\text{CO})(\text{PPh}_3)]$ (XIX), which is isolated as a yellow microcrystalline solid. Its IR spectrum shows three bands due to $\nu(\text{CO})$ arising from the overlapping of the two $\nu(\text{CO})$ characteristic of *cis*-Rh^{I} dicarbonyls attached to a rhodium(I) atom, (bands at 2080 and 2015 cm^{-1}) and one band due to $\nu(\text{CO})$ at 1995 cm^{-1} corresponding to a carbonyl group attached to the second rhodium atom.

TABLE 3
ANALYTICAL AND OTHER DATA FOR DINUCLEAR RHODIUM(I) COMPLEXES

Complex		Found (calcd.) (%)			Mol. weight	Yield (%)	Colour	ν(CO) (CH_2Cl_2) (cm^{-1})
		C	H	N				
X	$[(COD)Rh(\mu\text{-}Idz)_2CO)_2]$	48,4 (47,7)	3,8 (3,7)	9,2 (9,3)	607 (604)	76	orange	2080, 2020
XI	$[(TFB)Rh(\mu\text{-}Idz)_2Rh(CO)_2]$	45,9 (46,6)	2,3 (2,2)	7,8 (7,8)	767 (722)	96	orange	2080, 2015
XII	$[(NBD)Rh(\mu\text{-}Idz)_2Rh(CO)_2]$	47,2 (47,0)	3,5 (3,1)	9,2 (9,5)	599 (588)	46	orange	2080, 2010
XIII	$[(COD)Rh(\mu\text{-}Idz)_2Rh(TFB)]$	52,9 (52,7)	3,6 (3,6)	7,0 (7,2)	828 (774)	89	orange	-
XIV	$[(COD)Rh(\mu\text{-}Idz)_2Rh(NBD)]$	54,9 (54,4)	4,9 (4,7)	8,9 (8,75)	718 (640)	82	orange	-
XV	$[(TFB)Rh(\mu\text{-}Idz)_2Rh(NBD)]$	52,0 (52,3)	3,1 (3,2)	7,3 (7,4)	705 (758)	44	orange	-
XVI	$[(COD)Rh(\mu\text{-}Idz)_2Rh(CO)(PPh_3)]$	58,8 (58,7)	4,9 (4,45)	6,2 (6,7)	788 (839)	64	yellow	1980
XVII	$[(TFB)Rh(\mu\text{-}Idz)_2Rh(CO)(PPh_3)]$	55,3 (56,5)	3,5 (3,3)	5,7 (5,9)	881 (957)	81	orange	1987
XVIII	$[(NBD)Rh(\mu\text{-}Idz)_2Rh(CO)(PPh_3)]$	58,7 (58,4)	4,3 (4,0)	6,6 (6,8)	821 (822)	30	orange	1985
XIX	$[(CO)_2Rh(\mu\text{-}Idz)_2Rh(CO)(PPh_3)]$	53,7 (53,5)	3,5 (3,2)	6,7 (7,1)	732 (786)	50	yellow	2080, 2015, 1995

As expected, carbonylation in the presence of triphenylphosphine gives rise to the formation of $[(Ph_3P)(CO)Rh(\mu\text{-}Idz)]_2$ (IX).

Except for complex VII, all the complexes described are yellow or orange. This indicates that there are no inter- or intramolecular interactions between the metal centres [20].

Experimental

C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded (over the range 4000–200 cm^- on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets or dichloromethane solutions in cells with NaCl windows. Conductivities were measured with a Philips PW 9501/01 conductimeter in ca. $5 \times 10^{-4} M$ acetone solutions. Molecular weights were measured with a Perkin-Elmer 115 osmometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian FT 80A spectrometer using deuterochloroform as solvent. Chemical shifts are given in ppm downfield from TMS and 85% H_3PO_4 respectively. Positive signs indicate shifts to lower field. X-ray diffraction studies were carried out on powdered samples with a powder diffractometer Philips PW 1051.

Reactions were carried out at room temperature in air unless otherwise specified.

Preparation of complexes of the type $[(diolefin)Rh(HIdz)_2]ClO_4$ (I–III)

i) To solutions of complexes of the type $[Rh(diolefin)_2]ClO_4$ (0.30 mmol) in 15 ml of dichloromethane was added solid indazole (0.071 g, 0.60 mmol). The solutions were concentrated and diethyl ether added to precipitate complexes I–III, which are filtered off, washed with diethyl ether and air-dried.

ii) To acetone solutions of the species $[(diolefin)Rh(Me_2CO)_x]ClO_4$ (0.10 mmol) (prepared by treating $[(diolefin)Rh(\mu\text{-}Cl)]_2$ (0.05 mmol) in acetone with silver perchlorate (0.021 g, 0.10 mmol) for 15 min and subsequently removing the precipitated silver chloride) was added solid indazole (0.024 g, 0.20 mmol). The solutions were concentrated almost to dryness and diethyl ether was added to precipitate complexes I–III, which were filtered off, washed with diethyl ether and air-dried.

Reaction of $[(COD)Rh(HIdz)_2]ClO_4$ with KOH

To a methanol solution of $[(COD)Rh(HIdz)_2]ClO_4$ (0.058 g, 0.11 mmol) was added potassium hydroxide (0.11 mmol) in methanol. The orange-coloured complex $[(COD)Rh(\mu\text{-}Idz)]_2$, which separated immediately, was filtered off, washed with methanol/water (1/1) and vacuum-dried.

Reaction of $[(COD)Rh(\mu\text{-}Idz)]_2$ with $HClO_4$

To a dichloromethane solution of $[(COD)Rh(\mu\text{-}Idz)]_2$ (0.033 g, 0.05 mmol) was added solid indazole (0.012 g, 0.1 mmol) followed by perchloric acid (0.1 mmol). The resulting yellow solution was concentrated to 2 ml and diethyl ether was added to precipitate $[(COD)Rh(HIdz)_2]ClO_4$, The compound was filtered off, washed with diethyl ether and air-dried.

Preparation of $[(CO)_2Rh(HIdz)_2]ClO_4$

Carbon monoxide was bubbled for 20 min through a solution of

$[(COD)Rh(HIdz)_2]ClO_4$ (0.119 g, 0.22 mmol) in 5 ml of dichloromethane. 20 ml of hexane was added and the bubbling of carbon monoxide was continued for another 20 min. Upon stirring, the resulting oil gave a yellow solid which was filtered off, washed with hexane and vacuum-dried.

Preparation of complexes of the type $[(diolefin)Rh(\mu\text{-}Idz)]_2$ *(V–VII)*

To methanol suspensions of complexes of the type $[(diolefin)Rh(\mu\text{-}Cl)]_2$ (0.10 mmol) was added a mixture of indazole (0.024 g, 0.20 mmol) and triethylamine (28 μl, 0.2 mmol) in methanol. The resulting suspensions were stirred for 1 h, and the precipitated solids were filtered off, washed with large amounts of methanol/water (1/1) and vacuum-dried.

Preparation of $[(CO)_2Rh(\mu\text{-}Idz)]_2$ *(VIII)*

i) To a methanol suspension of $(CO)_2Rh(acac)$ (0.035 g, 0.13 mmol) was added solid indazole (0.016 g, 0.13 mmol). Addition of water to the resulting yellow solution gave a precipitate of the yellow complex VIII, which was filtered off, washed with methanol/water (1/1) and vacuum-dried.

ii) To a methanol suspension of $[(CO)_2Rh(\mu\text{-}Cl)]_2$ (0.040 g, 0.10 mmol) was added a mixture of indazole (0.024 g, 0.20 mmol) and triethylamine (28 μl, 0.20 mmol) in methanol. Workup was as in i).

Preparation of $[(Ph_3P)(CO)Rh(\mu\text{-}Idz)]_2$ *(IX)*

i) Carbon monoxide was bubbled for 15 min through a dichloromethane solution of $[(COD)Rh(\mu\text{-}Idz)]_2$ (0.037 g, 0.06 mmol). The presence of $[(CO)_2Rh(\mu\text{-}Idz)]_2$ in the solution was revealed by IR spectroscopy. Triphenylphosphine (0.029 g, 0.12 mmol) was added and the solution was concentrated. Addition of hexane gave a precipitate of complex IX, which was filtered off, washed with hexane and air-dried.

ii) A methanol suspension of $[(Ph_3P)(CO)Rh(\mu\text{-}Cl)]_2$ (0.022 g, 0.025 mmol) was treated with a mixture of indazole (0.006 g, 0.05 mmol) and sodium hydroxide (0.05 mmol) in methanol/water (5/5 ml). The solution was vacuum-concentrated to crystallize IX, which was filtered off, washed with methanol/water (1/1) and air-dried.

iii) Carbon monoxide was bubbled for 30 min through a dichloromethane solution of $[(COD)Rh(\mu\text{-}Idz)_2Rh(CO)(PPh_3)]$ (0.012 g, 0.014 mmol). Triphenylphosphine (0.004 g, 0.015 mmol) was added, the solution was concentrated and the complex was precipitated by adding hexane. The yellow solid was filtered off, washed with hexane and air-dried.

Preparation of $[(COD)Rh(\mu\text{-}Idz)_2Rh(CO)_2]$ *(X)*

i) A mixture of $[(CO)_2Rh(\mu\text{-}Idz)]_2$ (0.040 g, 0.07 mmol) and 1,5-cyclooctadiene (9 μl, 0.07 mmol) in dichloromethane was refluxed for 17 h, the reaction being monitored by IR spectroscopy. The solution was evaporated to dryness and the residue was treated with methanol, filtered off, washed with methanol and vacuum-dried.

ii) Carbon monoxide was bubbled for 30 min through a dichloromethane solution of $[(COD)Rh(\mu\text{-}Idz)]_2$ (0.126 g, 0.25 mmol). IR spectroscopy showed that $[(CO)_2Rh(\mu\text{-}Idz)]_2$ was the only carbonyl present in the solution. The solution was evaporated to dryness, and the residue was treated with methanol, filtered off, washed with methanol and vacuum-dried.

Preparation of complexes of the type [(diolefin)Rh(μ-Idz)$_2$Rh(CO)$_2$] (X–XII)

i) To dichloromethane solutions of complexes of the type [(diolefin)-Rh(HIdz)$_2$]ClO$_4$ (I–III) (0.10 mmol) was added (acac)Rh(CO)$_2$ (0.026 g, 0.10 mmol) followed by triethylamine (14 μl, 0.1 mmol). The mixture was stirred for 5 min and evaporated to dryness. The residue was extracted with methanol and filtered. Addition of a few drops of water to the filtrate gave precipitates of complexes X–XII, which were filtered off, washed with methanol/water and vacuum-dried.

ii) Solutions of the species [(Me$_2$CO)$_x$Rh(CO)$_2$]ClO$_4$ (0.1 mmol) (prepared by treating [(CO)$_2$Rh(μ-Cl)$_2$] (0.019 g, 0.05 mmol) with silver perchlorate (0.021 g, 0.1 mmol) in acetone under argon and removal of the precipitated silver chloride) were treated with acetone solutions of complexes of the type [(diolefin)Rh(HIdz)$_2$]ClO$_4$ (0.1 mmol). Addition of triethylamine (28 μl, 0.2 mmol) gave rise to a change in colour from yellow to orange, Work-up was continued as in i).

Preparation of complexes of the type [(diolefin)Rh(μ-Idz)$_2$Rh(diolefin')] (XIII–XV)

To acetone solutions of [(diolefin)Rh(HIdz)$_2$]ClO$_4$ (complexes I, II and III) (0.05 mmol) were added solutions of the species [(Me$_2$CO)$_x$Rh(diolefin')]ClO$_4$ (prepared by treating [(diolefin')Rh(μ-Cl)]$_2$ (0.025 mmol) with silver perchlorate (0.011 g, 0.05 mmol) in acetone) followed by triethylamine (14 μl, 0.10 mmol). The resulting orange solution was stirred for 5 min and then evaporated to dryness. The residue was extracted with methanol (15 ml) and water was added to the methanol extract to precipitate complexes XIII–XV, which were filtered off, washed with methanol/water (1/1) and vacuum-dried.

Preparation of complexes of the type [(diolefin)Rh(μ-Idz)$_2$Rh(CO)(PPh$_3$)] (XVI–XVIII)

i) To dichloromethane solutions of the complexes [(diolefin)Rh(HIdz)$_2$]ClO$_4$ (0.05 mmol) was added [(acac)Rh(CO)(PPh$_3$)] (0.025 g, 0.05 mmol) followed by triethylamine (7 μl, 0.05 mmol). The solutions were evaporated to dryness, and the residues were suspended in methanol then filtered off, washed with methanol/water (1/1) and vacuum-dried.

ii) To acetone solutions of the complexes [(diolefin)Rh(HIdz)$_2$]ClO$_4$ (0.05 mmol) was added [(Me$_2$CO)$_x$Rh(CO)(PPh$_3$)] (0.05 mmol) (obtained by treating [(Ph$_3$P)(CO)Rh(μ-Cl)]$_2$ (0.021 g, 0.025 mmol) for 30 min with silver perchlorate (0.011 g, 0.05 mmol) in acetone and removal of the silver chloride). Addition of triethylamine caused a change in colour from yellow to orange. The solution was evaporated to dryness and work-up was continued as in i).

Preparation of [(CO)$_2$Rh(μ-Idz)$_2$Rh(CO)(PPh$_3$)] (XIX)

Bubbling carbon monoxide for 5 min through a solution of [(COD)Rh(μ-Idz)$_2$Rh(CO)(PPh$_3$)] (0.031 g, 0.04 mmol) in 3 ml of dichloromethane and subsequent addition of 20 ml of methanol/water (1/1) with continued passage of the carbon monoxide stream for 1 h gave a yellow precipitate, which was filtered off, washed with methanol/water (1/1) and vacuum-dried.

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