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Inorganica Chimica Acta 347 (2003) 86–98
Inorganica Chimica Acta
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The rhodium and iridium co-ordination chemistry of the hemilabile hybrid ligand 1-(2′-pyridyl)-3-dimethylamino-2-propen-1-one

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Received 12 April 2002; accepted 22 July 2002

Dedication in honor Professor R. Usón

Abstract

Cationic mononuclear rhodium(I) or iridium(I) complexes of formula $[M(L_2)(N,O)]CF_3SO_3$ [M = Rh or Ir; L_2 = diolefin, $(CO)_2$ or $(CO)(PPh_3)$; N,O = 1-(2′-pyridyl)-3-dimethylamino-2-propen-1-one] have been prepared; the N,O hybrid ligand co-ordinates to the metal as a bidentate chelate group through the ketonic oxygen and the pyridine nitrogen. The reactivity of these complexes towards oxidative addition reactions of halogens, methyl iodide or triflic acid to afford octahedral rhodium(III) or iridium(III) species has also been studied. Addition of the N,O ligand to CH_2Cl_2 solutions of $[\{MCl(diolefin)\}_2]$ leads to the ion-pair complexes $[M(diolefin)(N,O)][MCl_2(diolefin)]$ (M = Rh or Ir; diolefin = 1,5-cyclooctadiene, COD, or tetrafluorobenzo-bicyclo(2,2,2)octatriene, TFB). The complexes have been characterised by analytical and spectroscopic data, their configuration has been confirmed by COSY and NOESY experiments and the structure of $[Rh(COD)(N,O)][RhCl_2(COD)]$ has been established by an X-ray diffraction study.

Keywords: Rhodium and iridium complexes; Chelate N,O ligands; Oxidative addition; Crystal structures

1. Introduction

The co-ordination of ligands containing different donor atoms to transition metals is well known and it has been the topic of many reports [1]. Among these ligands, of special interest are the 'hemilabile' hybrid ligands, i.e., ligands having one strong and one weak donor function [2]. Complexes with this type of ligands could be potential catalytic precursors; the chelate effect of the hemilabile ligand will confer stability to the catalyst precursors in the absence of the substrate and, on the other hand, they can easily produce a vacancy in the co-ordination of the metal — breaking the M-ligand bond at the weak donor atom — without complete dissociation. The interest in hemilabile N,O ligands [3] has been increasing recently and, as part of our current investigations into the chemistry of complexes with polifuntional ligands [4], we were interested in the synthesis of rhodium and iridium complexes incorporating N,O multidentate ligands. In the present study we have used the enaminone 1-(2′-pyridyl)-3-dimethylamino-2-propen-1-one (N,O) [5] which contains three donor atoms (Fig. 1) and consequently is capable of co-ordinate to metal atoms in several different ways.

On the other hand, the activation of organic substrates by organometallic complexes is a clear aim in the co-ordination chemistry field. In this way, the oxidative addition reactions, which imply the break of relatively inert bonds, represent one of the most fundamental processes in transition metal chemistry [6] and they play an invaluable role in many synthetic and catalytic reactions. An important point to force the complexes to experiment this type of reactions is that the metal maintains a relative high electron density. This aspect depends, among others factors, on the ligands bonded in the metal co-ordination sphere. The ligand N,O should favour these reactions since it has two σ donor atoms that can enlarge the nucleophilic character of the metal

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PII: S0020-1693(02)01449-4

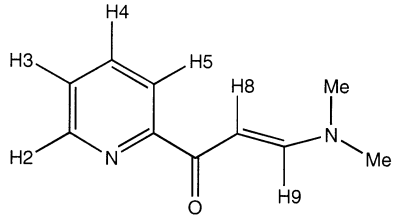


Fig. 1. Schematic drawing of the ligand 1-(2′-pyridyl)-3-dimethylamino-2-propen-1-one.

lowering the energy of the pathway to the transition state. The hemilabile character of the N,O ligand is also important since it can stabilise intermediates implicated in the oxidative addition reactions.

In this paper we describe the reactions of solvated cationic rhodium or iridium species $[M(L_2)(Me_2CO)_x]^+$ or the neutral dimers $[\{MCl(COD)\}_2]$ with the N,O ligand, 1-(2′-pyridyl)-3-dimethylamino-2-propen-1-one, which allow the preparation of new cationic square-planar rhodium and iridium(I) complexes as well as salts formed from two complex ions $[M(L_2)(N,O)][MCl_2(L_2)]$. We also report the oxidative addition reactions of some of these complexes with chlorine, iodine, methyl iodide or triflic acid to form octahedral rhodium(III) or iridium(III) products.

2. Results and discussion

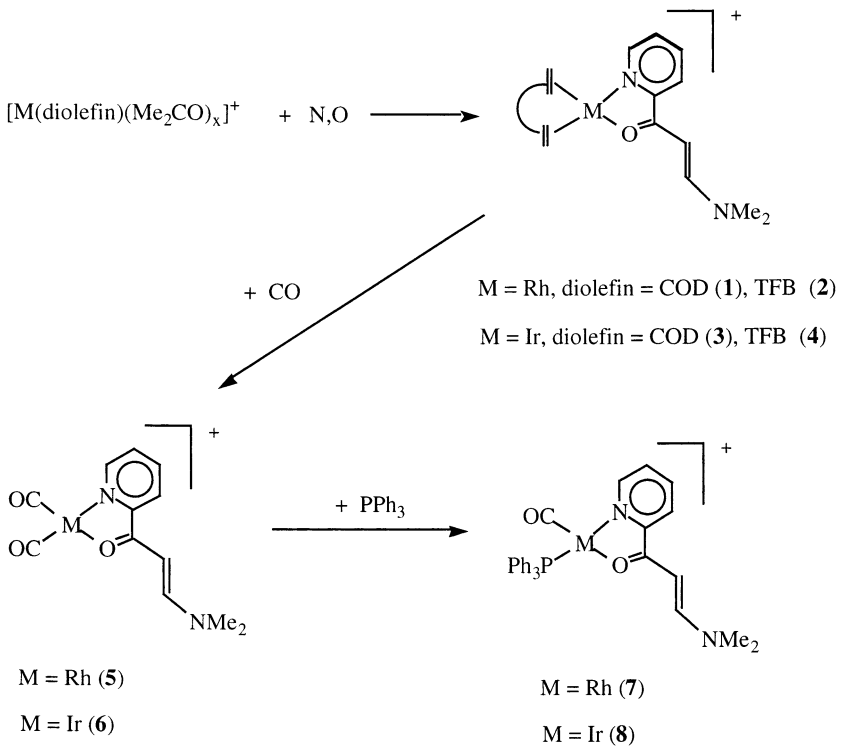
2.1. Rhodium(I) and iridium(I) complexes

A general route for the synthesis of cationic diolefin rhodium(I) or iridium(I) species involves the reaction of the solvated $[M(diolefin)(Me_2CO)_x]^+$ intermediate (prepared by the reaction of the dimers $[\{MCl(diolefin)\}_2]$ with Ag^+ and filtration of the AgCl formed) with neutral ligands. Thus, the reactions of acetone solutions of $[M(diolefin)(Me_2CO)_x]CF_3SO_3$ with N,O ligand in the stoichiometric ratio 1:1 produce the complexes $[M(diolefin)(N,O)]CF_3SO_3$ (**1**–**4**) (Scheme 1). Bubbling carbon monoxide through dichloromethane solutions of these complexes originates the displacement of the diolefin and the compounds $[M(CO)_2(N,O)]CF_3SO_3$ (M = Rh, **5**; Ir, **6**) are formed. Reaction of **5** or **6** with triphenylphosphine (1:1) results in the substitution of one CO molecule by PPh_3 affording $[M(CO)(PPh_3)(N,O)]CF_3SO_3$ (M = Rh, **7**; M = Ir, **8**).

Complexes **1**, **2**, **4**, **7** and **8** are stable in the solid state and in solution, while complexes **3**, **5** and **6** decompose in solution and can only be stored in the solid state at room temperature for a few hours. The analytical and MS data are consistent with a mononuclear formulation of the complexes. Their conductivity measures show the complexes to be 1:1 electrolytes in acetone and the infrared spectroscopic data indicate chelate co-ordination of the N,O ligand to the metal. In particular, the ν(C=O) frequencies of the co-ordinated ligand (see Section 3) are slightly shifted to lower frequencies from that of the free ligand (1643 cm^{-1} in CH_2Cl_2 solution). They occurred at similar frequencies to those reported previously for other N,O complexes [7]. The ^1H NMR spectra in $CDCl_3$ of compounds **1**–**4** showed the presence of the N,O ligand in addition to the co-ordinated diolefin (COD or TFB). Complexes **5** and **6** are scarcely soluble in common solvents. Both show two IR ν(CO) stretching bands in the 2000 cm^{-1} region (2095 and 2025 cm^{-1} for **5**, and 2081 and 2006 cm^{-1} for **6**), typical of *cis*-dicarbonyl derivatives of rhodium(I) or iridium(I) [8].

The diolefin complexes **1**–**4** are red, brown or orange in the solid state but they present the same colour in solution, while the dicarbonyl complexes **5** and **6** are yellow in solution but dark green in the solid state. This change of colour is paralleled by a marked change in the pattern of the carbonyl frequencies that becomes more complex, suggesting the presence of metal–metal interactions in the solid state, as previously observed for related complexes. Such interactions are possible due to the relative planarity of the whole complex molecule [9]. The intermetallic interactions disappear when these dicarbonyl complexes react with triphenylphosphine (1:1 ratio) to give the orange monocarbonyl complexes **7** and **8** (ν(CO) = 1983 cm^{-1} for **7**, and 1965 cm^{-1} for **8**). The ^{31}P NMR spectra of these compounds consist of a doublet, at δ 46.2 ppm with a J_{Rh-P} of 156.8 Hz for **7**, and a singlet at δ 20.2 ppm for **8**.

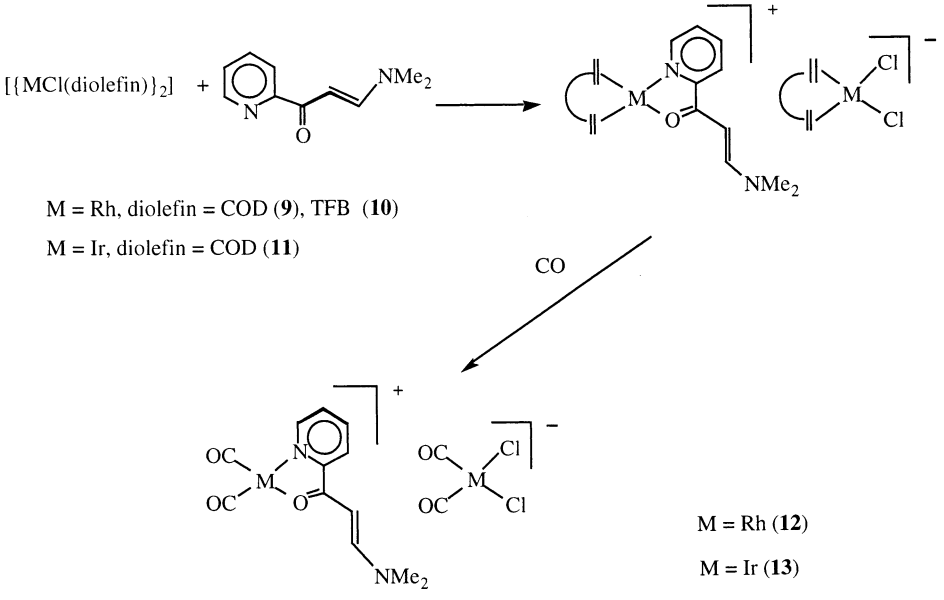
Attempts to prepare neutral rhodium or iridium complexes containing the 'RhCl(diolefin)' fragment prompted us to try the reaction of $[\{MCl(diolefin)\}_2]$ with the N,O ligand (Rh:(N,O) ratio 1:1) (Scheme 2). With M = Rh, dark red (**9**) and orange (**10**) compounds are obtained for the diolefin COD and TFB respectively, while for M = Ir and diolefin = COD, a brown compound (**11**) is prepared. The analytical results reveal the presence of only one molecule of ligand N,O for two metal atoms. The ^1H NMR spectra of the rhodium complexes (**9** and **10**) at low temperature, as well as that of the iridium compound (**11**) at room temperature, show two different types of diolefin in each complex. These spectra are characteristic of ion-pair species such as $[M(diolefin)(L_2)]^+$ $[MCl_2(diolefin)]^-$. This molecular structure has been confirmed by an X-ray structural determination of compound **9** (see below). At room temperature, the ^1H NMR spectra of **9** and **10** consist of broad signals for the diolefin and for the N,O ligand protons. This is indicative of the fluxionality of the compounds which, in solution, probably exist as an equilibrium among the ion-pair complexes and other neutral species; this fact would also explain the low conductivity observed for acetone solutions of the complexes (see Section 3) [10].



Scheme 1.

In the course of the reactions described above the N,O ligand has not suffered changes, apart from the redistribution of the electronic density by co-ordination to the metal. In contrast, the reaction of $[\{Rh(OY)(COD)\}_2]$ (Y = H, Me) with the enaminone ligand gives rise to an unexpected transformation of the ligand affording neutral complexes with the new anionic 1-(2′-pyridyl)-3-oxo-1-propenoxide ligand [11].

Bubbling carbon monoxide through dichloromethane solutions of any of **9**–**11** complexes makes the diolefin to be displaced and compounds **12** and **13** are obtained (Scheme 2). Compound **12** can also be prepared by reaction of $[\{RhCl(CO)_2\}_2]$ with N,O. The presence of four ν(CO) stretching bands for each compound in the terminal carbonyl region, two of which (2095 and 2025 cm^{-1} for **12**, and 2081 and 2006 cm^{-1} for **13**) at the



Scheme 2.

same frequencies than those of $[M(CO)_2(N,O)]^+$ (**5** and **6**) and the other two in similar positions to that described [12] for $[MCl_2(CO)_2]^-$ (M = Rh, at 2071 and 1994 cm^{-1}, M = Ir, at 2081 and 1975 cm^{-1}), is consistent with the ion-pair formulation of the complexes. **12** and **13** are not soluble enough to run their ^{13}C NMR; the conductivity of **12** is the expected for a 1:1 electrolyte, while **13** is not stable in solution.

2.2. Crystal and molecular structure of [Rh(COD)(N,O)][RhCl$_2$(COD)] (9)

The molecular structure of the two complex ions that form compound **9** is shown in Fig. 2, together with the numbering scheme used. Selected bond distances and angles are collected in Table 1. The crystal structure of **9** is built up with two different ionic rhodium complexes packed with no relevant interionic interactions, with the exception of two feeble Cl···H hydrogen bonds. These bonding interactions, H(4)···Cl(1) 2.951(2) Å and H(3)···Cl(2) 2.961(2) Å, are similar to the sum of the difficult-to-estimate Van der Waals radii (2.95 Å) [13], and are in the upper end of medium strength H···Cl–M hydrogens bonds (2.52–2.95 Å) [14]. They could account for the broad NMR signals detected and the slightly high values observed in the conductivity measurements of **9**, facts that suggest some kind of associative process in solution.

At each metal complex, both Rh atoms exhibit square planar environments with the cyclo-octadiene molecules co-ordinated in the usual 'tub' conformation and the olefins being bonded approximately perpendicular to the co-ordination planes. The maximum deviations from the co-ordination plane in each complex are 0.074(5) Å for the midpoint of the double bond C(16)–C(17) in the cation, and 0.125(6) Å for the olefin C(20)–C(21) in the anion.

Table 1
Selected bond lengths (Å) and bond angles (°) for compound **9**

Bond lengths			
Rh(1)–N(1)	2.101(4)	Rh(2)–Cl(1)	2.3895(12)
Rh(1)–O(1)	2.039(3)	Rh(2)–Cl(2)	2.3817(14)
Rh(1)–C(12)	2.129(3)	Rh(2)–C(20)	2.094(5)
Rh(1)–C(13)	2.125(4)	Rh(2)–C(21)	2.112(5)
Rh(1)–C(16)	2.108(5)	Rh(2)–C(24)	2.099(5)
Rh(1)–C(17)	2.097(5)	Rh(2)–C(25)	2.102(5)
N(1)–C(6)	1.366(6)	C(8)–C(9)	1.392(6)
C(6)–C(7)	1.496(6)	C(9)–N(2)	1.308(6)
C(7)–O(1)	1.283(5)	N(2)–C(10)	1.462(6)
C(7)–C(8)	1.386(6)	N(2)–C(11)	1.456(5)
Rh(1)–G(1)*	2.013(6)	Rh(2)–G(3)*	1.986(6)
Rh(1)–G(2)*	1.985(4)	Rh(2)–G(4)*	1.984(5)
Bond angles			
N(1)–Rh(1)–O(1)	78.87(13)	Cl(1)–Rh(2)–Cl(2)	89.94(5)
N(1)–Rh(1)–G(1)*	170.54(17)	Cl(1)–Rh(2)–G(3)*	92.08(16)
N(1)–Rh(1)–G(2)*	101.18(19)	Cl(1)–Rh(2)–G(4)*	177.54(17)
O(1)–Rh(1)–G(1)*	91.90(16)	Cl(2)–Rh(2)–G(3)*	175.62(17)
O(1)–Rh(1)–G(2)*	176.91(17)	Cl(2)–Rh(2)–G(4)*	90.15(18)
G(1)–Rh(1)–G(2)*	88.1(2)	G(3)–Rh(2)–G(4)*	88.0(2)
Rh(1)–N(1)–C(6)	113.1(3)	C(6)–C(7)–C(8)	122.0(4)
Rh(1)–O(1)–C(7)	117.2(3)	C(7)–C(8)–C(9)	117.8(4)
N(1)–C(6)–C(5)	121.0(4)	C(8)–C(9)–N(2)	128.1(4)
N(1)–C(6)–C(7)	114.1(4)	C(9)–N(2)–C(10)	122.6(4)
C(5)–C(6)–C(7)	124.8(4)	C(9)–N(2)–C(11)	122.0(3)
O(1)–C(7)–C(6)	116.5(4)	C(10)–N(2)–C(11)	115.3(4)
O(1)–C(7)–C(8)	121.4(4)		

*G(1), G(2), G(3) and G(4) represent the midpoints of the olefinic bonds C(12)–C(13), C(16)–C(17), C(20)–C(21) and C(24)–C(25), respectively.

In the cation, $[Rh(COD)(N,O)]^+$, the N,O ligand is co-ordinated as a bidentate chelate group through the ketonic oxygen and the pyridinic nitrogen, and forming a five-membered metallacycle with a bite angle of 78.87(14)°. This value is very low for a conventional

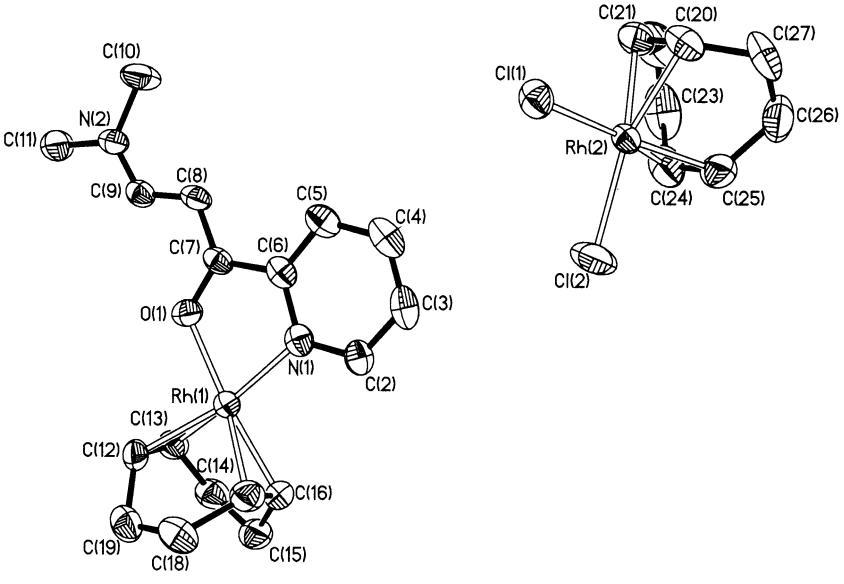


Fig. 2. Molecular structure of the two complex ions forming compound **9**.

square-planar complex, but similar to those reported for other related five-membered metallacycles containing related N,O donor groups linked to platinum group metals [15]. The Rh–N and the Rh–O bond distances are in the usual ranges described for square-planar cyclooctadiene rhodium(I) complexes [16]. However, on the other side, the Rh–C bond lengths observed in the cation are slightly different, reflecting the higher *trans* influence of the pyridinic nitrogen compared to that of the ketonic oxygen (see Table 1); this fact could be of relevance to understand the stereoselectivity in the substitution reactions of the dicarbonylic derivatives (see below).

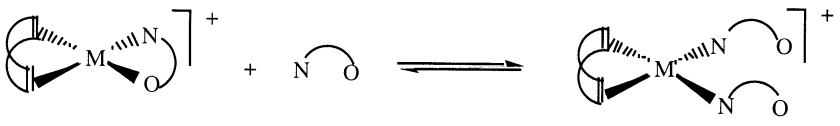
It is interesting to note that the whole hybrid N,O ligand in **9** exhibits a planar conformation — including the aminic N(2) nitrogen — with no atom deviation greater than 0.115(6) Å (C(11)), and coplanar with the metal co-ordination plane. It presents a *trans* configuration along the formal C(8)=C(9) double bond, contrasting with the *cis* configuration proposed for the original ligand [5].

As there is no X-ray study of the free N,O ligand, we have used the closely related ligand 1-[6-(4-pyrimidyl)-2′-pyridyl]-3-dimethylamino-2-propen-1-one (NON) — containing a pyrimidine substituent in the pyridine ring as the only structural difference [17] — to visualise the structural modifications of this N,O ligand after its co-ordination to the metal centre. From the data reported for the related NON molecule, we can conclude that the planarity of the aminic (N2) atom is present before and after ligand co-ordination. In both cases — free NON molecule and co-ordinated (N,O) ligand,— the bond distances observed along the O(1)–C(7)–C(8)–C(9)–N(2) chain show the existence of a clear electron density delocalization, implying the participation of the free electron pair of N(2) in this chain. This situation is more evident in the structure of **9** where the two C–C bond distances are statistically identical, C(7)–C(8) 1.386 and C(8)–C(9) 1.392(6) Å, intermediate between single and double bond, and where a significant elongation of the ketonic C=O double bond together with a marked shortening of the C(9)–N(2) single bond are also patent [18] (Table 1). All these facts allow us to understand the practical inertness of the aminic nitrogen of the N,O ligand towards metal co-ordination and the relative easy hydrolisis of the amine in the presence of traces of water [11].

As commented above the Rh(2) atom in the anion is square-planar co-ordinated; the molecular parameters of the anion are very similar to those reported for the same ionic moiety in related compounds and deserve no further comments [19].

2.3. Hemilabile behaviour of the N,O ligand

In the complexes described so far (**1**–**13**) the N,O ligand acts as a chelating bidentate ligand forming five membered metallacycles. In spite of the expected lability of the M–O bond, in the complexes described above this bond has not been broken by excess of CO or PPh_3. However, a way of proving the hemilabile behaviour of a ligand consists on the addition of the free ligand to a solution of a complex containing this ligand co-ordinated. So, upon addition of N,O to CH_2Cl_2 solution of compounds **1**–**3**, in molar ratio 1:1, species formulated as $[ML_2(N,O)_2]^+$ are formed (Eq. (1))



(1)

These species could not be isolated and they were characterised only in solution. The assignment of their structure is based on the following evidences: (a) The ^1H NMR spectra reveals that the coupling constants between the olefinic protons H8–H9, of ca. 12 Hz, are intermediate between that of the free ligand (12.6 Hz) and those of the starting complexes **1**–**3** (around 11 Hz). This can be interpreted in terms of the different C–C and C–N bond order when the ligand is acting as chelate, monodentate or when it is uncoordinated. Acting as chelate, the N,O ligand has a high delocalization of the electron density (see X-ray structure of **9**) so the C8–C9 bond must have only partial double bond character and the coupling constant J_{H8-H9} decreases. (b) The ^1H NMR spectra of $[ML_2(N,O)_2]^+$ are temperature dependent. Rising the temperature broadens the signals of the Me groups of the ligand as it also happens with the free ligand. However, the electron density delocalization produced with the N,O chelation, in complexes **1**–**3**, gives a partial double bond character to the C–N bond, so the rotation around this bond is highly restricted.

Despite several attempts, it was impossible to isolate these cationic bis(N,O)-complexes. With diethyl ether,

the starting complexes precipitate and the free ligand remains in solution. With hexane, the obtained solid is a mixture of the starting product and the free ligand so the IR spectra of the solid is the superposition of both spectra. By washing this mixture with diethyl ether, they separate again giving complexes **1**–**3** and the ligand.

When the ancillary ligands L_2 are $(CO)_2$ or $(CO)(PPh_3)$ no reaction was observed. The spectroscopic data indicate that in solution, as well as in the solid state, there is only a mixture of the starting rhodium or iridium products and the free N,O ligand.

2.4. Rhodium(III) and iridium(III) complexes

Oxidative addition reactions of halogen (chlorine or iodine) or methyl iodide to the square-planar complexes **1**–**8** give octahedral rhodium(III) or iridium(III) compounds. The assignment of proton resonances in different fragments was obtained by combining information from ^{1}H COSY and ^{1}H NOESY NMR experiments which also provided the stereochemistry of the formed isomers.

2.4.1. Reactions with chlorine

Compounds **1** and **3** react with chlorine to give rhodium(III) or iridium(III) complexes. Treatment of CH_2Cl_2 solutions of **1** or **3**, at ambient temperature, with the stoichiometrically required amount of solid $Cl_2 \cdot IC_6H_5$ affords the stable, rather insoluble, orange complexes $[MCl_2(N,O)(COD)]\ CF_3SO_3$ (M = Rh, **14**; M = Ir, **15**). In both reactions the oxidative addition is stereospecific and the formed isomer is that in which the distribution of the chlorine atoms is *cis*, since complexes **14** and **15** show, in the ^{1}H NMR, four resonances for the four olefinic protons of the diolefin. NOESY experiments confirm that the only obtained isomer is the *cis* isomer and that one of the chlorine atoms is *trans* to the O atom. The mass spectrum (FAB positive) of **15** shows the parent peak of the cation $[IrCl_2(N,O)(COD)]$ (*m*/*z* 547) while for complex **14** only the peak at *m*/*z* 574, due to the fragment $[RhCl(N,O)(COD)(CF_3SO_3)]$, has been identified. The reaction with chlorine of complexes **2** and **4**–**8** gives solids of very low solubility and their NMR spectra indicate that mixtures of unidentified products are present.

2.4.2. Reactions with iodine

The complexes **3**, **7** and **8** react smoothly with iodine giving stable metal(III) compounds in good yields. The oxidative addition of iodine (1:1 molar ratio) to CH_2Cl_2 or acetone solutions of complex $[Ir(COD)(N,O)]CF_3SO_3$ (**3**) gives a mixture of the *cis* and the *trans* addition products $[IrI_2(COD)(N,O)]CF_3SO_3$ (**16a** and **16b**) either if the stoichiometric amount or an excess of iodine is used. With **7** and **8**, the reaction with iodine produces orange solids of $[MI_2(CO)(PPh_3)(N,O)]$ (CF_3SO_3) (M = Rh, **17**, M = Ir, **18**). In both reactions, only one isomer is present according to the spectroscopic data although the stereochemistry of the products cannot be unequivocally assigned by NMR due to the absence of protons in three of the ligands. The ν(CO) appears at 2093 cm^{-1} for **17** and 2056 cm^{-1} for **18**. The ^{1}H NMR of the complexes shows the H2 protons as triplets by the coupling with the P atoms and the H3 protons while the irradiation of P changes the triplet into a doublet. These data indicate that the P atom and the N atoms must be *trans* in these complexes, so the complexes can be either the *trans* isomers or the *cis* isomers with the iodine *trans* to the O atom. The ^{31}P NMR spectra of these compounds consist of a doublet at δ 29.6 ppm with a J_{Rh-P} of 94.9 Hz, for **17**, and a singlet at δ −6.9 ppm for **18**. The mass spectra (FAB positive) show the parent peak [*M*] and the peaks [*M*–CO] and [*M*−CO−I] for **17** and [*M*−I], [*M*−CO−I] and [*M*−I_2] for **18**.

2.4.3. Reactions with methyl iodide

The reactivity of the complexes **1**–**6** towards CH_3I has been checked. Rhodium compounds **1** or **2** do not react even by using an excess of CH_3I or heating the toluene solution at refluxing temperature, while the iridium analogues **3** and **4** react at ambient temperature giving octahedral iridium(III) compounds. The reaction of **3** with MeI produces the compound $[Ir(CH_3)I(COD)(N,O)]CF_3SO_3$ (**19a**) in which NOE experiments show that a *trans* addition has taken place. This compound slowly isomerizes in solution: after 24 h a mixture of a new *cis* isomer (**19b**), with the methyl group in a *trans* position to the oxygen atom (75%), and the *trans* (**19a**) (25%) addition product occurs. No further progress in the isomerization process has been observed, even heating the solution, avoiding the isolation of the pure *cis* isomer. The TFB complex, **4**, gives the *trans* addition product $[Ir(CH_3)I(TFB)(N,O)]CF_3SO_3$ (**20**) that does not isomerize even by heating its acetone solution at refluxing temperature or by UV irradiation. The methyl groups appear as singlets in the ^{1}H NMR spectra at δ 2.0 for **19b**, 2.6 for **19a** and 2.4 ppm for **20**. The mass spectra (FAB positive) of these complexes show the parent peaks [*M*] and peaks corresponding to [*M*−I] and [*M*−Me−I].

The dicarbonyl complexes **5** and **6** also react with MeI showing different behaviour for Rh and Ir compounds. Treatment of compound **5** in acetone, at refluxing temperature, gives $[Rh(CH_3)I(CO)_2(N,O)]CF_3SO_3$ (**21a**). This compound shows only one absorption band in solution in the IR spectrum in the 2000 cm^{-1} region for both CO groups, at 2075 cm^{-1}, so the CO groups should be in mutually *trans* positions. NOE experiments indicate that the methyl group (at δ 1.8 ppm, d, J_{Rh-H} = 2.4 Hz) is *trans* to the nitrogen atom and the iodine is *trans* to the O atom. If this reaction is

carried out at room temperature and using CH_2Cl_2 as solvent the IR spectrum shows, together with the absorptions of the starting complex **5** (at 2095 and 2025 cm^{-1}), two new ν(CO) bands assigned to a new complex **21b**. One of these bands at 1726 cm^{-1} corresponds to an acyl group and the other, at 2093 cm^{-1}, is due to a terminal CO group. For five days the intensity of these bands increases at the same time than those of the starting complex decreases and a new one, assigned to **21a**, appears at 2075 cm^{-1}. When the absorptions of the starting product disappear, the mixture isolated is **21a** and **21b** in a 40:60 ratio. **21b** can not be isolated pure but can be identified by its spectroscopic data as $[Rh(COMe)I(N,O)(CO)]CF_3SO_3$.

For the reaction of the iridium complex **6** with MeI, only the compound $[Ir(CH_3)I(CO)_2(N,O)]CF_3SO_3$ (**22**) has been obtained. No acyl formation has been observed during the reaction, which is in agreement to the higher tendency of the rhodium to form acyl complexes**.** The IR spectrum of **22** shows the ν(CO) bands at 2134 and 2082 cm^{-1}, while the ^1H NMR spectrum gives the methyl group as a singlet at 1.5 ppm.

*2.4.4. Reaction of [Ir(CO)(PPh3)(N,O)]CF3SO3 (**8**) with trifluoromethylsulfonic acid*

The reaction of triflic acid with CH_2Cl_2 solutions of **8** at −60 °C leads to the oxidative addition of the product in 15 min. The reaction can be monitored by IR spectroscopy. The ν(CO) band of the new product appears at 2064 cm^{-1}. The solution is concentrated at low temperature and the addition of hexane leads to a mononuclear hydride iridium(III) compound $[Ir(H)(OSO_2CF_3)(CO)(PPh_3)(N,O)]CF_3SO_3$ (**23**). The ν(Ir–H) band is not observed in the IR spectrum but the presence of a doublet at −22.4 ppm ($J_{H-P} = 15.6$ Hz) in the ^1H NMR confirms the existence of the hydride ligand. This signal is typical for a terminal hydride *cis* to a phosphine. This position is confirmed by the NOE spectrum, which shows a small contact between them. The NOE spectrum also indicates that *trans* to the O atom there is a ligand without protons (CO or OSO_2CF_3) and that the P atom should be in *trans* position to the pyridinic nitrogen, as deduced from the coupling between H2 and the phosphorus (9.0 ppm, J = 4.0 Hz). The ^{19}F NMR spectrum displays two singlets, one sharp at −80.4 and a broad one at −80.6 ppm, which indicate that only one of the anions is co-ordinated to the iridium. Acetone solutions of **23** display molar conductivity values halfway between 1:1 and 2:1 electrolytes, suggesting that the acetone solvent molecules may displace the co-ordinated triflate ligand. The ^{31}P NMR shows a singlet at δ 3.0 and in the MS the molecular ion peak can be observed.

3. Experimental

All solvents were distilled and dried by standard methods [20]. The reactions were carried out under an argon atmosphere by standard Schlenk techniques. ^1H, ^{13}C, ^{31}P and ^{19}F nuclear magnetic resonance spectra were recorded with Varian Gemini 2000, Varian Unity 300 or Bruker ARX 300 spectrometers. Chemical shifts are reported in ppm and the solvents were used as internal reference. Infrared spectra (4000–400 cm^{-1}) were recorded on a Nicolet 550 or on a Perkin–Elmer 883 (4000–200 cm^{-1}) spectrophotometers using Nujol mulls between polyethylene sheets or in solution in NaCl cells. Elemental analyses were carried out with a Perkin–Elmer 240 C microanalyser. The FAB mass spectra (m-nitrobenzyl alcohol matrix) were recorded in a V.G. Autoespec double-focusing mass spectrometer operating in the positive mode; high resolution mass spectra are in accordance with the simulated isotopic pattern distribution. The starting materials (N,O) ligand [5], $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$ [21], $[\{Rh(\mu\text{-}OMe)(COD)\}_2]$ [22], $[\{Ir(\mu\text{-}Cl)(COD)\}_2]$ [23], $[\{Ir(\mu\text{-}OMe)(COD)\}_2]$ [24], $[\{Rh(\mu\text{-}Cl)(TFB)\}_2]$ [25], $[IrCl(TFB)_2]$ [26] and $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ [27], were prepared according to the reported methods.

*3.1. Preparation of [M(diolefin)(N,O)]CF3SO3 (M = Rh, diolefin = COD, **1**; M = Rh, diolefin = TFB, **2**; M = Ir, diolefin = COD, **3**; M = Ir, diolefin = TFB, **4**)*

To CH_2Cl_2/acetone solutions (10/5 ml) of $[\{MCl(diolefin)\}_2]$ (0.43 mmol), for complexes **1**–**3**, or $[IrCl(TFB)_2]$ (0.83 mmol) for complex **4**, $AgCF_3SO_3$ (222 mg, 0.86 mmol) was added. After 30 min at room temperature (r.t.) for complexes **1**–**3**, or 1 h at refluxing temperature for **4**, the white formed solid (AgCl) was filtered off, and the ligand N,O (150 mg, 0.86 mmol) was added to the solution. The mixtures were stirred for 10 min at r.t. Partial evaporation of the solvent and addition of diethyl ether led to the precipitation of compounds **1**–**4** which were filtered off, washed with diethyl ether and vacuum dried. Data for **1**: yellow, yield 98%. *Anal*. Calc. for $C_{19}H_{24}F_3N_2O_4RhS$: C, 42.55; H, 4.51; N, 5.22; S, 5.97. Found: C, 42.51; H, 4.38; N, 5.18; S, 5.97%. MS (FAB) *m/e* 387 [M^+, 100]. Λ_M (acetone, $C = 5.0 \times 10^{-4}$ mol l^{-1}): 130 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (20 °C, $CDCl_3$) δ ppm: 8.6 (d, $^3J_{H-H} = 8.1$ Hz, H–5), 8.1 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-9), 8.1 (t, $^3J_{H-H} = 6.9$ Hz, 1H, H-4), 7.6 (d, $^3J_{H-H} = 5.4$ Hz, 1H, H-2), 7.5 (t, $^3J_{H-H} = 6.4$ Hz, 1H, H-3), 6.4 (d, $^3J_{H-H} =$ 11.4 Hz, 1H, H-8), 4.3 (br, 4H, =CH), 3.4 (s, 3H, NMe), 3.3 (s, 3H, NMe), 2.5 (m, 4H, CH_2), 1.9 (m, 4H, CH_2). ^{13}C {H} NMR ($CDCl_3$) δ ppm: 186.7 (s, C-7), 160.0 (s, C-9), 157.1 (s, C-6), 147.5 (s, C-2), 140.3 (s, C-4), 128.2 (s, C-3), 126.1 (s, C-5), 120.8 (q, $^1J_{C-F} = 324.5$ Hz, Otf), 91.9 (s, C-8), 47.1 (s, NMe), 39.1 (s, NMe), 30.12 (s,

CH_2). Data for **2**: Orange; yield 95%. *Anal*. Calc. for $C_{23}H_{18}F_7N_2O_4RhS$: C, 42.22; H, 2.77; N, 4.28; S, 4.89. Found: C, 42.06; H, 3.04; N, 4.23; S, 4.12%. MS (FAB) *m/e* 505 [M^+, 100]. Λ_M (acetone, $C = 5.0 \times 10^{-4}$ mol l^{-1}): 123 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (20 °C, $CDCl_3$) δ ppm: 8.6 (d, $^3J_{H-H} = 8.0$ Hz, 1H, H-5), 8.2 (d, $^3J_{H-H} =$ 11.4 Hz, 1H, H-9), 8.0 (m, H-4), 7.5 (2H, H-2 + H-3), 6.4 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-8), 5.7 (m, 2H, TFB), 4.0 (m, 4H, TFB), 3.4 (s, 3H, NMe), 3.3 (s, 3H, NMe). ^{19}F NMR ($CDCl_3$) δ ppm: −80.6 (s, 1F, Otf), −149.1 (m, 2F, TFB), −161.1 (m, 2F, TFB). Data for **3**: Brown; yield 92%. *Anal*. Calc. for $C_{19}H_{24}F_3IrN_2O_4S$: C, 36.47; H, 3.87; N, 4.48; S, 5.12. Found: C, 36.14; H, 3.23; N, 4.39; S, 5.03%. MS (FAB) *m/e* 477 [M^+, 100], 626 (MOtf; 5). ^1H NMR (20 °C, $CDCl_3$) δ ppm: 8.8 (d, $^3J_{H-H} = 8.1$Hz, 1H, H-5), 8.3 (d, $^3J_{H-H} = 11.4$Hz, 1H, H-9), 8.2 (t, $^3J_{H-H} = 7.8$Hz, 1H, H-4), 7.9 (d, $^3J_{H-H} =$ 4.8Hz, 1H, H-2), 7.6 (t, $^3J_{H-H} = 6.6$Hz, 1H, H-3), 6.6 (d, $^3J_{H-H} = 11.4$Hz, 1H, H-8), 4.5 (br, 2H, =CH), 3.7 (br, 2H, =CH), 3.4 (s, 3H, NMe), 3.4 (s, 3H, NMe), 2.3(m, 4H, CH_2), 1.7 (m, 4H, CH_2). ^{13}C {H} NMR ($CDCl_3$) δ ppm: 187.9 (s, C-7), 160.9 (s, C-9), 158.2 (s, C-6), 147.9 (s, C-2), 141.3 (s, C-4), 128.8 (s, C-3), 126.6 (s, C-5), 120.8 (q, $^1J_{C-F} = 324.5$ Hz, Otf), 93.1 (s, C-8), 47.6 (s, Me), 39.7 (s, NMe), 31.1 (s, CH_2). Data for **4**: Brown; yield 69%. *Anal*. Calc. for $C_{23}H_{18}F_7IrN_2O_4S$: C, 37.15; H, 2.44; N, 3.77; S, 4.30. Found: C, 37.53; H, 2.08; N, 3.70; S, 4.12%. MS (FAB) *m/e* 505 [M^+, 100]. Λ_M (acetone, $C = 5.0 \times 10^{-4}$ mol l^{-1}): 101 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (20 °C, $CDCl_3$) δ ppm: 8.7 (d, $^3J_{H-H} = 8.0$ Hz, 1H, H-5), 8.7 (d, $^3J_{H-H} = 11.0$ Hz, 1H, H-9), 8.4 (t, $^3J_{H-H} = 8.0$ Hz, 1H, H-4), 8.0 (d, $^3J_{H-H} = 5.5$ Hz, 1H, H-2), 7.8 (t, $^3J_{H-H} = 6.6$ Hz, 1H, H-3), 6.6 (d, $^3J_{H-H} =$ 11.4 Hz, H-8), 5.8 (br, 2H, TFB), 3.7 (s, 3H, NMe), 3.5 (s, 3H, NMe), 3.4 (br, 4H, TFB). ^{19}F NMR ($CDCl_3$) δ ppm: −79.2(s, 1F, Otf), −148.2 (m, 2F, TFB), −160.2 (m, 2F, TFB).

3.2. Preparation of $[M(CO)_2(N,O)]CF_3SO_3$ ($M = Rh$, **5**; $M = Ir$, **6**)

Through CH_2Cl_2 (15 ml) solutions of **1** or **3** (0.14 mmol) CO (1 atm, r.t.) was bubbled for 1 h; complexes **5** and **6** were formed as green solids, which were separated by filtration, washed with diethyl ether and vacuum dried. Both complexes are scarcely soluble in most solvents and they have to be store under argon to avoid decomposition. Data for **5**: Green; yield 67%. *Anal*. Calc. for $C_{13}H_{12}F_3N_2O_6RhS$: C, 32.25; H, 2.50; N, 5.80; S, 6.61. Found: C, 31.35; H, 2.12; N, 5.66; S, 6.36%. IR (CH_2Cl_2, cm^{-1}): ν(CO): 2095 and 2025. MS (FAB) *m/e* 335 [M^+, 100], 307 [$(M-CO)^+$, 55]. Λ_M (acetone, $C = 5.0 \times 10^{-4}$ mol l^{-1}): 106 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 9.0 (d, $^3J_{H-H} = 8.1$ Hz, 1H, H-5), 8.5 (d, $^3J_{H-H} = 4.8$ Hz, 1H, H-2), 8.3 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-9), 8.3 (t, H-4), 7.6 (m, 1H, H-3), 6.8 (d, $^3J_{H-H} =$ 11.4 Hz, 1H, H-8), 3.5 (s, 3H, NMe), 3.5 (s, 3H, NMe). Data for **6**: Green; yield 86%. *Anal*. Calc. for $C_{13}H_{12}F_3IrN_2O_6S$: C, 27.23; H, 2.11; N, 4.88; S, 5.59. Found: C, 27.17; H 1.89; N 4.74; S 5.26%. IR (CH_2Cl_2, cm^{-1}): ν(CO): 2081 and 2006. MS (FAB) *m/e* 425 [M^+, 100], 395 [$(M-CO)^+$, 5], 365 [$M-(CO)_2^+$, 10]. Λ_M (acetone, $C = 5.0 \times 10^{-4}$ mol l^{-1}): 99 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 9.1 (d, $^3J_{H-H} = 8.1$ Hz, 1H, H-5), 8.7 (d, $^3J_{H-H} = 5.4$ Hz, 1H, H-2), 8.4 (d, $^3J_{H-H} =$ 11.1 Hz, 1H, H-9), 8.3 (t, $^3J_{H-H} = 7.8$ Hz, 1H, H-4), 7.7 (t, $^3J_{H-H} = 6.3$ Hz, 1H, H-3), 7.0 (d, $^3J_{H-H} = 11.4$ Hz. 1H, H-8), 3.6 (s, 3H, NMe_2), 3.6 (s, 3H, NMe_2).

3.3. Preparation of $[M(CO)(PPh_3)(N,O)]CF_3SO_3$ ($M = Rh$, **7**; $M = Ir$, **8**)

To CH_2Cl_2 (10 ml) suspensions of **5** (34 mg, 0.071 mmol) or **6** (42 mg, 0.073 mmol) PPh_3 (20 mg, 0.076 mmol) was added and the solutions stirred for 10 min. Evaporation to 2 ml and addition of diethyl ether (10 ml) led to orange solids, **7** and **8**, which were separated by filtration, washed with diethyl ether and vacuum dried. Data for **7**: Orange; yield 81%. *Anal*. Calc. for $C_{30}H_{27}F_3N_2O_5PRhS$: C, 50.15; H, 3.79; N, 3.90; S, 4.46. Found: C, 50.50; H, 3.24; N, 3.94; S, 3.78%. IR (CH_2Cl_2, cm^{-1}): ν(CO): 1983. MS (FAB) *m/e* 569 [M^+, 100], 541 [$(M-CO)^+$, 10].]. Λ_M (acetone, $C = 5.0 \times 10^{-4}$ mol l^{-1}): 106 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 8.7 (d, $^3J_{H-H} = 6.3$ Hz, 1H, H-2), 8.7 (d, $^3J_{H-H} = 8.4$ Hz, 1H, H-5), 8.2 (t, $^3J_{H-H} = 7.8$ Hz, 1H, H-4), 7.7–7.4 (16H, PPh_3 + H-3), 7.1 (d, $^3J_{H-H} =$ 11.4 Hz, 1H, H-9), 6.4 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-8), 3.3 (s, 3H, NMe), 3.3 (s, 3H, NMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ ppm: 46.2 (d, $^1J_{Rh-P} = 156.8$ Hz). ^{13}C {H} NMR ($CDCl_3$) δ ppm: 189.6 (d, $^2J_{C-Rh} = 76.0$ Hz, 1H, CO), 185.9 (s, C-7), 159.7 (s, C-9), 155.4 (s, C-6), 151.3 (s, C-2), 140.2 (s, C-4), 134.2 (d, $^3J_{C-P} = 11.5$Hz, C_{ortho}), 131.2 (d, $^3J_{H-H} = 48.8$Hz, 1C, C_{ipso}), 131.0 (s, C_{para}), 128.7 (d, $^3J_{C-P} = 10.1$ Hz, C_{meta}), 128.0 (s, C-3), 126.7 (s, C-5), 120.9 (q, $^1J_{C-F} = 321.5$ Hz, Otf), 92.9 (s, C-8), 46.8 (s, NMe), 39.1 (s, NMe). Data for **8**: Orange; yield 68%. *Anal*. Calc. for $C_{30}H_{27}F_3IrN_2O_5PS$: C, 44.61; H, 3.37; N, 3.47; S, 3.97. Found: C, 44.75; H, 2.93; N, 3.23; S, 3.33%. IR (CH_2Cl_2, cm^{-1}): ν(CO): 1967. MS (FAB) *m/e* 659 [M^+, 100], 629 [$(M-CO)^+$, 10]. Λ_M (acetone, $C = 5.0 \times 10^{-4}$ mol l^{-1}): 112 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 8.8 (d, $^3J_{H-H} = 5.4$ Hz, 1H, H-2), 8.7 (d, $^3J_{H-H} = 8.1$ Hz, 1H, H-5), 8.2 (td, $^3J_{H-H} =$ 7.8 Hz, $^4J_{H-H} = 1.5$, 1H, H-4), 7.7–7.3 (16H, PPh_3 + H-3), 7.1 (d, $^3J_{H-H} = 11.1$ Hz, 1H, H-9), 6.5 (d, $^3J_{H-H} =$ 11.7 Hz, 1H, H-8), 3.3 (s, 3H, NMe), 3.2 (s, 3H, NMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ ppm: 20.2 s. ^{13}C {H} NMR ($CDCl_3$) δ ppm: 186.9 (s, C–O or C-7), 173.5 (br, C-7 or C–O), 161.0 (s, C-9), 155.1 (s, C-6), 150.9 (s, C-2), 140.5 (s, C-4), 134.5 (d, $^2J_{C-P} = 11.5$ Hz, C_{ortho}), 131.2 (d, $^1J_{C-P} = 60.4$ Hz, C_{ipso}), 131.1 (s, C_{para}), 129.4 (s, C-3),

128.6 (d, $^3J_{C-P} = 11.1$ Hz, C_{meta}), 127.4 (s, C-5), 120.9 (q, $^1J_{C-F} = 324.5$ Hz, Otf), 94.3 (s, C-8), 47.4 (s, NMe), 39.9 (s, NMe).

3.4. Preparation of [M(diolefin)(N,O)][MCl$_2$-(diolefin)] (M = Rh, diolefin = COD, **9**; M = Rh, diolefin = TFB, **10**; M = Ir, diolefin = COD, **11**)

To CH_2Cl_2 solutions of [{MCl(diolefin)}$_2$] (0.50 mmol) solid N,O (90 mg, 0.52 mmol) was added. After 1 h stirring, the solutions were concentrated to 1 ml. The addition of diethyl ether (10 ml) led to solids, **9**, **10** and **11**, which were separated by filtration, washed with diethyl ether and vacuum dried. Data for **9**: dark red; yield 97%. *Anal*. Calc. for $C_{26}H_{36}Cl_2N_2ORh_2$: C, 46.66; H, 5.42; N, 4.19. Found: C, 46.22; H, 5.09; N, 4.22%. MS (FAB) *m/e* 387 [M^+, 100]. Λ_M (acetone): 31 Ω^{-1} cm^2 mol^{-1}. Λ_M (methanol): 68 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$, −50 °C) δ ppm: 8.9 (d, $^3J_{H-H} = 8.1$ Hz, 1H, H-5), 8.3 (t, $^3J_{H-H} = 6.9$ Hz, 1H, H-4), 8.1 (d, $^3J_{H-H} = 11.3$ Hz, 1H, H-9), 7.7 (br, H-2), 7.5 (t, $^3J_{H-H} = 6.1$ Hz, 1H, H-3), 6.7 (d, $^3J_{H-H} = 11.2$ Hz, 1H, H-8), 4.2 (br, 4H, =CH), 4.2 (br, 4H, =CH), 3.4 (s, 3H, NMe), 3.4 (s, 3H, NMe), 2.4 (m, 8H, CH_2), 1.9 (m, 4H, CH_2), 1.6 (br, 4H, CH_2). ^{13}C {H} NMR ($CDCl_3$, −50 °C) δ ppm: 186.4 (s, C-7), 159.4 (d, C-9), 157.2 (s, C-6), 147.0 (s, C-2), 140.9 (s, C-4), 127.7 (s, C-3), 127.3 (s, C-5), 93.4 (s, C-8), 81.0 (br, =CH), 78.5 (br, =CH), 47.3 (s, NMe), 40.5 (s, NMe), 30.8 (s, CH_2), 30.2 (s, CH_2). Data for **10**: Orange; yield 73%. *Anal*. Calc. for $C_{34}H_{24}Cl_2F_8N_2ORh_2$: C, 45.11; H, 2.67; N, 3.09. Found: C, 44.11; H, 2.86; N, 3.01%. MS (FAB+) *m/e* 505 [M^+, 100]; (FAB−) *m/e* 399 [M^-, 85]. Λ_M (acetone): 55 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$, −40 °C) δ ppm: 8.8 (d, $^3J_{H-H} = 7.6$ Hz, 1H, H-5), 8.3 (t, $^3J_{H-H} = 7.4$ Hz, 1H, H-4), 8.2 (d, $^3J_{H-H} = 11.0$ Hz, 1H, H-9), 7.7 (br, H-2), 7.6 (t, $^3J_{H-H} = 6.0$ Hz, 1H, H-3), 6.6 (d, $^3J_{H-H} = 11.7$ Hz, 1H, H-8), 5.6 (br, 2H, TFB), 5.4 (br, 2H, TFB), 3.9 (br, 4H, TFB), 3.6 (br, 4H, TFB), 3.4 (s, 3H, NMe), 3.4 (s, 3H, NMe). ^{19}F NMR ($CDCl_3$ −40 °C) δ ppm: −148.4 (br, 2F), −160.7 (br, 2F). ^{13}C {H} NMR ($CDCl_3$ −40 °C) δ ppm: 186.4 (s, C-7), 159.8 (s, C-9), 156.1 (s, C-6), 148.8 (s, C-2), 141.3 (br, C-4), 128.0 (s, C-3), 126.8 (br, C-5), 93.2 (s, C-8), 55.4 (s, =CH), 49.5 (s, NMe), 40.2 (d, =CH), 39.2 (s, NMe). Data for **11**: Brown; yield 87%. *Anal*. Calc. for $C_{26}H_{36}Cl_2Ir_2N_2O$: C, 36.83; H, 4.28; N, 3.30. Found: C, 36.76; H, 4.25; N, 3.34%. IR (Nujol, cm^{-1}): ν(Ir–Cl) 285. MS (FAB+) *m/e* 477 [M^+, 100]; (FAB−) *m/e* 371 [M^-, 20]. Λ_M (acetone): 43 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 9.2(d, $^3J_{H-H} = 7.1$ Hz, 1H, H-5), 8.4 (t, $^3J_{H-H} = 6.9$ Hz, 1H, H-4), 8.3 (d, $^3J_{H-H} = 11.2$ Hz, 1H, H-9), 8.0 (br, H-2), 7.6 (t, $^3J_{H-H} = 6.2$ Hz, 1H, H-3), 6.9 (d, $^3J_{H-H} = 10.8$ Hz, 1H, H-8), 4.1 (br, 4H, =CH), 3.9 (br, 4H, =CH), 3.5 (s, 3H, NMe), 3.4 (s, 3H, NMe), 2.3 (m, 4H, CH_2), 2.1(m, 4H, CH_2), 1.7(m, 4H, CH_2), 1.3 (m, 4H, CH_2). ^{13}C {H} NMR ($CDCl_3$) δ ppm: 187.9 (s, C-7), 160.7 (br, C-9), 158.4 (s, C-6), 147.3 (br, C-2), 142.0 (s, C-4), 128.5, 128,4 (C-3+C-5), 95.1 (s, C-8), 65.4 (br, =CH), 59.7 (br, =CH), 47.8 (s, NMe), 41.6 (s, NMe), 31.9 (s, CH_2), 31.2 (s, CH_2).

3.5. Preparation of [M(CO)$_2$)(N,O)][MCl$_2$(CO)$_2$] (M = Rh, **12**; M = Ir, **13**)

Through CH_2Cl_2 (10 ml) solutions of **9** or **10** (0.18 mmol) CO (1 atm, r.t.) was bubbled for 50 min; complexes **12** and **13** were forming as green solids. To complete the precipitation of the complexes hexane was added to the solution while the CO bubbling continues for another 30 min. The solids were filtered off under argon atmosphere, washed with diethyl ether and vacuum dried. Both complexes are not stable to the air or to the temperature so they have to be kept under argon and in the fridge. Compound **13** is not soluble enough to run its NMR spectra. Data for **12**: Green; yield 65%. *Anal*. Calc. for $C_{14}H_{12}Cl_2N_2O_5Rh_2$: C, 29.76; H, 2.14; N, 4.96. Found: C, 29.37; H, 1.73; N, 4.98%. IR (CH_2Cl_2, cm^{-1}): ν(CO): 2095, 2071, 2025, 1994. MS (FAB) *m/e* 355 [M^+, 100], 307 [$(M-CO)^+$, 20], 279 [$M-(CO)_2$, 15]. Λ_M (acetone, $C = 5.0 \times 10^{-4}$ mol l^{-1}): 97 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 8.9 (d, $^3J_{H-H} = 8.3$ Hz, 1H, H-5), 8.5 (d, $^3J_{H-H} = 5.3$ Hz, 1H, H-2), 8.4 (td, $^3J_{H-H} = 7.9$ Hz, $^4J_{H-H} = 1.3$ Hz, 1H, H-4), 8.3 (d, $^3J_{H-H} = 11.3$ Hz, 1H, H-9), 7.7 (t, $^3J_{H-H} = 6.5$ Hz, 1H, H-3), 6.6 (d, $^3J_{H-H} = 11.3$ Hz, 1H, H-8), 3.6 (s, 3H, NMe), 3.5 (s, 3H, NMe). ^{13}C {H} NMR (CD_2Cl_2) δ ppm: 186.1 (s, C-7), 184.4 (br, CO), 183.4 (br, CO), 182.6 (br, CO), 181.6 (br, CO), 161.7 (br, C-9), 156.4 (s, C-6), 153.2 (br, C-2), 142.6 (s, C-4), 129.5 (C-3), 127.3 (s, C-5), 94.4 (s, C-8), 48.4 (s, NMe), 40.9 (s, NMe). Data for **13**: Green; yield 62%. *Anal*. Calc. for $C_{14}H_{12}Cl_2Ir_2N_2O_5$: C, 22.61; H, 1.63; N, 3.77. Found: C, 23.28; H, 2.42; N, 2.77%. IR (CH_2Cl_2, cm^{-1}): ν(CO): 2081, 2058, 2006, 1975. MS (FAB) *m/e* 425 [M^+, 25), 397 [$(M-CO)^+$, 10], 366 [$M-(CO)_2$, 15].

3.6. Preparation of cis-[MCl$_2$(COD)(N,O)]CF$_3$SO$_3$ (M = Rh, **14**; M = Ir, **15**)

To CH_2Cl_2 solutions (10 ml) of **1** (43 mg, 0.08 mmol) or **3** (50 mg, 0.08 mmol) solid $Cl_2 \cdot IC_6H_5$ (23 mg, 0.084 mmol) was added. After 1 h stirring, the solutions were concentrated to 2 ml. The addition of diethyl ether (10 ml) led to solids, **14** and **15**, which were separate by filtration, washed with diethyl ether and vacuum dried. Data for **14**: Orange; yield 74%. *Anal*. Calc. for $C_{19}H_{24}Cl_2F_3N_2O_4RhS$: C, 37.58; H, 3.98; N, 4.61; S, 5.27. Found: C, 36.84; H, 3.09; N, 4.61; S, 5.40%. MS (FAB) *m/e* 574 [RhCl(N,O)(COD)Otf, 10]. Λ_M (acetone, $C = 5.0 \times 10^{-4}$ mol l^{-1}): 107 Ω^{-1} cm^2 mol^{-1}. ^{1}H

NMR (20 °C, $CDCl_3$) δ ppm: 9.6 (d, $^3J_{H-H} = 5.7$ Hz, 1H, H-2), 8.9 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-9), 8.7 (d, $^3J_{H-H} = 7.9$ Hz, 1H, H-5), 8.4 (td, $^3J_{H-H} = 7.8$ Hz, $^4J_{H-H} = 1.5$ Hz 1H, H-4), 8.0 (ddd, $^3J_{H-H} = 7.5$ Hz, $^3J_{H-H} = 5.9$ Hz, $^4J_{H-H} = 1.5$ Hz, 1H, H-3), 6.8 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-8), 6.6 (m, 1H, =CH), 6.1 (m, 1H, =CH), 5.9 (m, 1H, =CH), 5.4 (m, 1H, =CH), 3.7 (s, 3H, NMe), 3.5 (s, 3H, NMe), 3.2–2.3 (8H, CH_2). Data for **15**: Orange; yield 81%. *Anal*. Calc. for $C_{19}H_{24}Cl_2F_3IrN_2O_4$: C, 32.76; H, 3.47; N, 4.02; S, 4.60. Found: C, 32.52; H, 2.87; N, 3.85; S, 4.59%. MS (FAB) *m/e* 547 [M^+, 100]. Λ_M (acetone, $C = 5.0 \times 10^{-4}$ mol l^{-1}): 100 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (20 °C, $CDCl_3$) δ ppm: 9.5 (d, $^3J_{H-H} = 5.5$ Hz, 1H, H-2), 8.6 (d, $^3J_{H-H} = 8.4$ Hz, 1H, H-5), 8.5 (d, $^3J_{H-H} = 11.6$ Hz, 1H, H-9), 8.2 (td, $^3J_{H-H} = 7.8$ Hz, $^4J_{H-H} = 1.5$ Hz, 1H, H-4), 7.8 (t, $^3J_{H-H} = 6.1$ Hz, 1H, H-3), 6.5 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-8), 6.4 (m, 1H, =CH), 6.1 (m, 1H, =CH), 5.7 (m, 1H, =CH), 4.9 (m, 1H, =CH), 3.6 (s, 3H, NMe), 3.4 (s, 3H, NMe), 3.2 (8H, CH_2).

3.7. Preparation of *cis*-[$IrI_2(COD)(N,O)$]CF_3SO_3 (**16**)

To CH_2Cl_2 (10 ml) suspensions of the iridium(I) compound **3** an excess of iodine (ratio 2:3) was added and the solution stirred for 2 h. Concentration to a volume of 1 ml and addition of diethyl ether afforded a brown solid which was filtered off, washed with Et_2O and dried. Yield 90%. The solid obtained is a mixture of the *trans* and the *cis* addition isomers in a 1:1 ratio. *Anal*. Calc. for $C_{19}H_{24}F_3I_2IrN_2O_4S$: C, 25.95; H, 2.75; N, 3.18; S, 3.64. Found: C, 25.06; H, 2.86; N, 3.24; S, 3.22%. IR (nujol, cm^{-1}): ν(CO) ketone: 1632. MS (FAB) *m/e* 731 [M^+, 75), 604 [(M-I)$^+$, 15], 477 [$(M-I_2)^+$, 100]. Λ_M (acetone): 110 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (20 °C, $CDCl_3$) *cis*-isomer, **16a**, δ ppm: 10.2 (d, $^3J_{H-H} = 4.8$ Hz, 1H, H-2), 8.6 (d, $^3J_{H-H} = 7.6$ Hz, 1H, H-5), 8.4 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-9), 8.1, 7.6 (t, H-3), 6.4 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-8), 6.3 (m, 1H, =CH), 6.2 (m, 1H, =CH), 5.8 (m, 1H, =CH), 4.5 (m, 1H, =CH), 3.6 (s, 3H. NMe), 3.4 (s, 3H. NMe), 3.2–1.0 (8H, CH_2). ^{1}H NMR (20 °C, $CDCl_3$) *trans*-isomer, **16b**, δ ppm: 8.8 (d, $^3J_{H-H} = 7.8$ Hz, 1H, H-5), 8.2 (d, $^3J_{H-H} = 11.2$ Hz, 1H, H-9), 8.1 (t, H-4), 7.9 (d, $^3J_{H-H} = 5.3$ Hz, 1H, H-2), 7.6 (t, H-3), 6.7 (d, $^3J_{H-H} = 11.1$ Hz, 1H, H-8), 6.0 (m, 2H, =CH), 5.6 (m, 2H, =CH), 3.5 (s, 3H, NMe), 3.4 (s, 3H, NMe), 3.2–1.0 (8H, CH_2).

3.8. Preparation of [$MI_2(CO)(PPh_3)(N,O)$]CF_3SO_3 ($M = Rh$, **17**; $M = Ir$, **18**)

To CH_2Cl_2 solutions (10 ml) of **7** (50 mg, 0.07 mmol) or **8** (50 mg, 0.062 mmol) solid I_2 (50 mg, 0.20 mmol) was added. After 30 m stirring, the solutions were concentrated to 3 ml. The addition of diethyl ether (10 ml) led to solids, **17** and **18**, which were separated by filtration, washed with diethyl ether and vacuum dried. Data for **17**: Orange; yield, 81%. *Anal*. Calc. for $C_{29}H_{27}F_3I_2N_2O_4PRhS$: C, 37.06; H, 2.80; N, 2.88; S, 3.30. Found: C, 35.65; H, 3.01; N, 2.59; S, 3.10%. IR (CH_2Cl_2, cm^{-1}): ν(CO) ketone: 1632; ν(CO): 2081, 2093. MS (FAB) *m/e* 823 [M^+, 30), 795 [$(M-CO)^+$, 20], 668 [$(M-ICO)^+$, 50], 569 [$(M-I_2)^+$, 100]. Λ_M (acetone): 98.9 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (20 °C, $CDCl_3$) δ ppm: 8.9 (d, $^3J_{H-H} = 7.6$ Hz, 1H, H-5), 8.2 (t, $^3J_{H-H} = 5.0$ Hz, 1H, H-2), 8.2 (t, $^3J_{H-H} = 7.8$ Hz, 1H, H-4), 8.0–7.8 (m, 6H, PPh_3), 7.7 (d, $^3J_{H-H} = 11.7$ Hz, 1H, H-9), 7.6 (t, $^3J_{H-H} = 5.7$ Hz, 1H, H-3), 7.6-7.3 (m, 9H, PPh_3), 6.8 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-8), 3.5 (s, 3H, NMe), 3.4 (s, 3H, NMe). ^{31}P{^{1}H} NMR ($CDCl_3$) δ ppm: 29.6 (d, $J_{Rh-P} = 94.9$ Hz). ^{13}C {H} NMR($CDCl_3$) δ ppm: 185.6 (s, C-7), 179.9 (s, CO), 160.6 (s, C-9), 155.6 (s, C-6), 152.5 (s, C-2), 141.2 (s, C-4), 134.3 (d, $^1J_{C-F} =$ 9.8Hz, C_{meta}), 132.1 (s, C_{para}), 131.0 (d, $^1J_{C-F} = 59.6$ Hz, C_{ipso}), 129.5 (s, C-3), 128.6 (d, $^1J_{C-F} = 11.3$ Hz, C_{ortho}), 128.3 (s, C-5), 96.9 (s, C-8), 47.8 (s, NMe), 40.31 (s, NMe). Data for **18**: Orange; yield, 54%. *Anal*. Calc. for $C_{29}H_{27}F_3I_2IrN_2O_4PS$: C, 33.94; H, 2.56; N, 2.64; S, 3.02. Found: C, 34.57; H, 2.90; N, 1.86; S, 3.25%. IR (CH_2Cl_2, cm^{-1}): ν(CO) ketone: 1638; ν(CO): 2056. MS (FAB) *m/e* 913 [M^+, 60], 786 [$(M-CO)^+$, 15], 757 [$(M-ICO)^+$, 20], 659 [$(M-I_2)^+$, 50]. Λ_M (acetone): 108.5 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (20 °C, $CDCl_3$) δ ppm: 8.8 (d, $^3J_{H-H} = 8.2$ Hz, 1H, H-5), 8.8 (t, $^3J_{H-H} =$ 4.1 Hz, 1H, H-2), 8.2 (t, $^3J_{H-H} = 6.9$ Hz, 1H, H-4), 7.8 (6H PPh_3), 7.7 (t, $^3J_{H-H} = 6.9$ Hz, 1H, H-3), 7.5 (9H, PPh_3), 7.2 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-9), 6.6 (d, $^3J_{H-H} = 11.4$ Hz, 1H, H-8), 3.4 (s, 3H, NMe), 3.4 (s, 3H, NMe). ^{31}P{^{1}H} NMR ($CDCl_3$), δ ppm: −6.9 (s). ^{13}C {H} NMR ($CDCl_3$) δ ppm: 184.3 (C-7+C-O), 160.7 (s, C-9), 158.5 (d, $^3J_{C-P} = 11.9$ Hz, C-2), 156.2 (s, C-6), 151.4 (s), 141.5 (s, C-4), 134.6 (d, $^3J_{C-P} = 9.1$ Hz, C_{meta}), 131.9 (d, $^4J_{C-P} = 3.0$ Hz, C_{para}), 129.6 (d, $^1J_{C-P} = 41.4$ Hz, C_{ipso}), 128.5 (d, $^2J_{C-P} = 11.5$ Hz, C_{ortho}), 96.9 (s, C-8), 47.7 (s, NMe), 40.3 (s, NMe).

3.9. Preparation of [$IrMeI(COD)(N,O)$]CF_3SO_3 (**19**)

To a brown CH_2Cl_2 (10 ml) suspension of compound **3** (50 mg, 0.080 mmol) MeI (0.5 ml, 8.0 mmol) was added and the mixture was stirred for 1 hour. Concentration of the solution to a volume of 1 ml and addition of diethyl ether afforded an orange solid, **19a**, which was filtered off, washed with Et_2O and dried. Yield 73%. NOESY experiments show that **19a** is the product of a *trans* addition of MeI to compound **3**. If the reaction is kept stirring for several hours the *cis* addition product isomer, **19b**, starts forming. After 24 h the reaction product is a mixture of **19a** and **19b** in a ratio 1:3. This proportion does not change anymore by heating,

prolonging the reaction time or by UV irradiation. *Anal*. Calc. for $C_{20}H_{27}F_3IIrN_2O_4S$: C, 31.29; H, 3.55; N, 3.65; S, 4.18. Found: C, 30.61; H, 3.55; N, 3.48; S, 3.85%. MS (FAB) *m/e* 619 [M^+, 100], 491 [$(M-I)^+$, 35], 477 [$(M-MeI)^+$, 60]. Λ_M (acetone): 109.6 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (20 °C, $CDCl_3$) isomer **19a**, δ ppm: 8.9 (d, $^3J_{H-H}=8.1$ Hz, 1H, H-5), 8.2 (d, $^3J_{H-H}=11.4$ Hz, 1H, H-9), 8.2 (t, $^3J_{H-H}=7.5$ Hz, 1H, H-4), 7.8 (d, $^3J_{H-H}=5.1$ Hz, 1H, H-2), 7.6 (t, $^3J_{H-H}=7.2$ Hz, 1H, H-3), 6.7 (d, $^3J_{H-H}=11.4$ Hz, 1H, H-8), 5.6 (m, 1H, =CH), 5.1(m, 1H, =CH), 4.7(m, 1H, =CH), 4.2(m, 1H, =CH), 3.43 (s, 3H, NMe), 3.40 (s, 3H, NMe), 4.0–2.0 (8H, CH_2), 2.0 (s, 3H, Me–Ir). Isomer **19b**, δ ppm: 8.7 (d, $^3J_{H-H}=7.8$ Hz, 1H, H-5), 8.6 (d, $^3J_{H-H}=5.4$ Hz, 1H, H-2), 8.4 (d, $^3J_{H-H}=11.7$ Hz, 1H, H-9), 8.1 (t, $^3J_{H-H}=7.5$ Hz, 1H, H-4), 7.2 (t, $^3J_{H-H}=5.7$ Hz, 1H, H-3), 6.5 (d, $^3J_{H-H}=11.7$ Hz, 1H, H-8), 5.8 (m, 1H, =CH), 4.9 (m, 1H, =CH), 4.4 (m, 1H, =CH), 3.9 (m, 1H, =CH), 3.4 (s, 3H, NMe), 3.3 (s, 3H, NMe), 2.8–1.4 (8H, CH_2), 2.6 (s, 3H, Me–Ir).

3.10. Preparation of *[IrMeI(TFB)(N,O)]CF_3SO_3 (20)*

The procedure was the same as that for **19a** and **19b**, but only the product of the *trans* addition of MeI to compound **4** is obtained. Orange; yield 84%. *Anal*. Calc. for $C_{24}H_{21}F_7IIrN_2O_4S$: C, 32.55; H, 2.39; N, 3.16; S, 3.62. Found: C, 32.63; H, 2.68; N, 3.25; S, 3.60%. MS (FAB) *m/e* 737 [M^+, 100], 609 [$(M-I)^+$, 35], 595 [$(M-MeI)^+$, 40]. Λ_M (acetone): 109.6 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (20 °C, $CDCl_3$) δ ppm: 8.7 (d, $^3J_{H-H}=7.8$ Hz, 1H, H-5), 8.3 (d, $^3J_{H-H}=11.4$ Hz, 1H, H-9), 8.1 (t, $^3J_{H-H}=7.5$ Hz, 1H, H-4), 7.9 (d, $^3J_{H-H}=5.1$ Hz, 1H, H-2), 7.6 (t, $^3J_{H-H}=6.6$ Hz, 1H, H-3), 6.6 (d, $^3J_{H-H}=11.4$ Hz, 1H, H-8), 6.0 (m, 1H, TFB), 5.6 (m, 1H, TFB), 5.5 (t, $^3J_{H-H}=5.1$ Hz, 1H, TFB), 5.0 (t, $^3J_{H-H}=4.8$ Hz, 1H, TFB), 4.6 (t, $^3J_{H-H}=5.1$, TFB), 4.4 (t, $^3J_{H-H}=4.8$ Hz, 1H, TFB), 3.4 (s, 3H, NMe), 3.4 (s, 3H, NMe), 2.3 (s, 3H, Me–Ir). ^{19}F NMR (HDA), δ ppm: −80.2 (s, 1F, Otf), −148.0 (m, 2F, TFB), −161.2 (m, 2F, TFB).

3.11. Preparation of *[RhMeI(CO)$_2$(N,O)]CF_3SO_3, (21a) and [Rh(COMe)I(CO)(N,O)] CF_3SO_3, (21b)*

To an acetone (10 ml) suspension of compound **5** (90 mg, 0.19 mmol) MeI (0.6 ml, 9.6 mmol) was added and the mixture was stirred at reflux temperature for 45 min. After working up the solution, an orange solid, **21a**, is obtained. If the solvent is CH_2Cl_2 and the reaction mixture is stirred at r.t., IR spectra of the solution showed that an acyl band at 1726 cm^{-1} is turning up and the ν(CO) bands of compound **5** are disappearing. The reaction is very slow, so before the ν(CO) bands of compound **5** have disappeared completely, the IR spectrum showed the absorptions of compound **21a**. After 5 days the solution is a mixture of complexes **21a** and **21b** in a ratio 3:2. It has not been possible to isolate pure compound **21b**. Data for **21a**: Orange; yield 70%. *Anal*. Calc. for $C_{14}H_{15}F_3IN_2O_6RhS$: C, 26.86; H, 2.41; N, 4.47; S, 5.12. Found: C, 26.74; H, 1.43; N, 4.37; S, 4.51%. IR (CH_2Cl_2, cm^{-1}): ν(CO): 2075. MS (FAB) *m/e* 477 [M^+, 5], 449 [$(M-CO)^+$, 100], 421 [$(M-(CO)_2)^+$, 5], 329 [$(M-I)^+$, 35], 307 [$(M-MeI)^+$, 90]. Λ_M (acetone): 98.1 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (20 °C, $CDCl_3$) δ ppm: 9.0 (d, $^3J_{H-H}=5.7$ Hz, 1H, H-2), 8.7 (H-5+H-9), 8.4 (t, $^3J_{H-H}=7.9$ Hz, 1H, H-4), 7.9 (t, $^3J_{H-H}=6.6$ Hz, 1H, H-3), 6.6 (d, $^3J_{H-H}=11.1$ Hz, 1H, H-8), 3.7 (s, 3H, NMe), 3.5 (s, 3H, NMe), 1.8 (d, $^3J_{Rh-H}=2.4$ Hz, 1H, 3H, Me–Rh). Data for **21b**: Orange. IR (CH_2Cl_2, cm^{-1}): ν(CO): 2093; ν(COMe): 1726. ^{1}H NMR (20 °C, $CDCl_3$) δ ppm: 9.1 (d, H-2), 8.8 (d, H-9), 8.6 (H-5), 8.4 (t, H-4), 7.9 (t, H-3), 6.7 (d, H-8), 3.7 (s, 3H, NMe), 3.5 (s, 3H, NMe), 2.7 (s, 3H, COMe).

3.12. Preparation of *[IrMeI(CO)$_2$(N,O)]CF_3SO_3 (22)*

To CH_2Cl_2 (10 ml) solution of compounds **6** (90 mg, 0.19 mmol) an excess of MeI (0.6 ml, 9.6 mmol) was added and the mixtures were stirred at r.t. for 3.5 h. After working up the solution, solid **22** was obtained. Orange; yield 63%. *Anal*. Calc. for $C_{14}H_{15}F_3IIrN_2O_6S$: C, 23.50; H, 2.11; N, 3.92; S, 4.48. Found: C, 26.25; H, 2.50; N, 6.17; S, 4.54%. IR (CH_2Cl_2, cm^{-1}): ν(CO): 2134, 2082. MS (FAB) *m/e* 567 [M^+, 100]. Λ_M (acetone): 100.8 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (20 °C, $CDCl_3$) δ ppm: 9.3 (d, $^3J_{H-H}=5.7$ Hz, 1H, H-2), 8.8 (H-5+H-9), 8.5 (t, $^3J_{H-H}=8.1$Hz, 1H, H-4), 8.0 (m, H-3), 6.8 (d, $^3J_{H-H}=10.8$ Hz, 1H, H-8), 3.7 (s, 3H, NMe), 3.5 (s, 3H, NMe), 1.5 (s, 3H, Me–Ir).

3.13. Preparation of *[Ir(H)(CF_3SO_3)(CO)(PPh_3)(N,O)]CF_3SO_3 (23)*

A solution of compound **8** (250 mg, 0.31 mmol) in 15 ml of CH_2Cl_2 was cooled at −60 °C and triflic acid (27 ml, 0.31 mmol) was slowly added. The solution was stirred for 15 min and the solvent was partially removed at low temperature. Slow diffusion in the freezer of a layer of hexane into the solution afforded a yellow mycrocrystalline solid **23**. Yield 66%. Data for **23**: *Anal*. Calc. for $C_{31}H_{27}F_6IrN_2O_8PS_2$: C, 38.87; H, 2.84; N, 2.92; S, 6.69. Found: C, 39.07; H, 3.49; N, 2.84; S, 6.32%. IR (CH_2Cl_2, cm^{-1}): ν(CO): 2064. MS (FAB) *m/e* 809 [M^+, 30], 659 [$(M-Otf)^+$, 100]. Λ_M (acetone): 153.3 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (20 °C, $CDCl_3$) δ ppm: 9.0 (t, $^3J_{H-H}=4.0$ Hz, 1H, H-2), 8.7 (d, $^3J_{H-H}=8.1$ Hz, 1H, H-5), 8.0 (t, $^3J_{H-H}=8.2$ Hz, 1H, H-4), 7.7 (t, $^3J_{H-H}=6.4$ Hz, 1H, H-3), 7.6–7.4 (15H, PPh_3), 7.2 (d, $^3J_{H-H}=10.8$ Hz, H-9), 6.5 (d, $^3J_{H-H}=11.1$ Hz, 1H, H-8), 3.4 (s, 3H, NMe), 3.3 (s, 3H, NMe), −22.4 (d, $^2J_{P-H}=15.6$ Hz, 1H, H$^-$). ^{19}F NMR (20 °C, $CDCl_3$)

Table 2
Crystal data and structure refinement parameters for compound **9**

Empirical formula	$C_{26}H_{36}Cl_2N_2ORh_2$
Formula weight	669.29
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.7819(9)
b (Å)	11.1220(10)
c (Å)	12.0352(10)
α (°)	79.4843(12)
β (°)	68.9462(12)
γ (°)	75.1615(13)
V (Å^3)	1295.39(19)
Z	2
D_{calc} (g cm^{-3})	1.716
μ (mm^{-1})	1.502
Crystal size (mm^3)	$0.41 \times 0.39 \times 0.10$
θ_{max} (°)	1.82–23.26
Index ranges	$-11 \le h \le 11$, $-8 \le k \le 12$, $-13 \le l \le 13$
Reflections measured	4936
Independent reflections	3531 [$R_{int} = 0.0363$]
Max. and min. transmission	0.840 and 0.531
Data/restraints/parameters	3531/0/299
Goodness-of-fit on F^2	1.160
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0303$, $wR_2 = 0.0684$
R indices (all data)	$R_1 = 0.0337$, $wR_2 = 0.0712$
Largest difference peak and hole (e Å^{-3})	0.359 and −0.370

δ ppm: −80.4 (s, 1F), −80.6 (br, 1F). $^{31}P\{^1H\}$ NMR (20 °C, $CDCl_3$) δ ppm: 3.0 (s).

3.14. X-ray crystallography

Suitable dark red crystals for the X-ray study were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of complex **9**. A summary of crystal data and refinement parameters is reported in Table 2. Data were obtained at 153(2)K from a Bruker SMART CCD area detector diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using narrow frames (0.3° in ω). Cell parameters were refined from the observed setting angles and detector positions of strong reflections. During data collection instrument and crystal stability was evaluated from measurement of equivalent reflections at different measuring times; no important variations were observed. Intensities were integrated from several series of exposure frames covering almost a complete spherical reciprocal space [28]. Data were corrected for Lorentz and polarisation effects, and a semi-empiricial absorption correction (min. and max. transmission factor 0.531 and 0.840) based on the repeated and symmetry-equivalent reflections, was also applied [29].

The structure was solved by Patterson method and completed by successive difference Fourier syntheses. Anisotropic thermal parameters were included for all non-hydrogen atoms. Hydrogen atoms were found in the difference maps — except those bonded to C(26) which were included in calculated positions — and were refined with riding positional and displacement parameters. Refinements were carried out by full-matrix least-squares on F^2 for all data [30]. Final agreement factors are collected in Table 2. Residual peaks in the final difference map were 0.356 and −0.370 e Å^{-3}. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement programs [30].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 182764. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

A.P.M. is thankful for a grant from DGES. The generous financial support from DGES (project PB98-1598) is gratefully acknowledged.

References

[1] (a) J.A. Davies, F.R. Hartley, Chem. Rev. 81 (1981) 79;
(b) G.R. Newkome, Chem. Rev. 93 (1993) 2067;
(c) Z.Z. Zang, H. Cheng, Coord. Chem. Rev. 147 (1996) 1;
(d) P. Espinet, K. Soulantika, Coord. Chem. Rev. 195 (1999) 499.
[2] C.S. Slone, D.A. Wienberger, C.A. Mirkin, Prog. Inorg. Chem. 48 (1999) 233.
[3] (a) K.G. Orrell, A.G. Osborne, V. Sik, M.W. da Silva, Polyhedron 14 (1995) 2797;
(b) C.A. Otter, D.A. Bardwell, S.M. Couchman, J.C. Jeffery, J.P. Maher, M.D. Ward, Polyhedron 17 (1998) 211;
(c) S.K. Bertilsson, L. Tedenborg, D.A. Alonso, P.G. Andersson, Organometallics 18 (1999) 1281;
(d) R.J. Anderson, P.H. Hagback, P.J. Steel, Inorg. Chim. Acta 284 (1999) 273;
(e) A. Neves, S.M. de M. Romanowski, I. Vencato, A.S. Mangrich. J. Chem. Soc., Dalton Trans. 1998, 617;
(f) G. Minghetti, S. Stoccoro, M.A. Cinellu, A. Zucca, M. Manassero, M. Sansoni, J. Chem. Soc., Dalton Trans. (1998) 4119.
[4] (a) L.A. Oro, M.A. Ciriano, J.J. Pérez-Torrente, B.E. Villarroya, Coord. Chem. Rev. 193 (1999) 941;
(b) D. Carmona, C. Vega, F.J. Lahoz, R. Atencio, L.A. Oro, M.P. Lamata, F. Viguri, E. San José, Organometallics 19 (2000) 2273;
(c) C. Tejel, M.A. Ciriano, J.A. López, F.J. Lahoz, L.A. Oro, Angew. Chem., Int. Ed. Engl. 37 (1998) 1542;
(d) A. Elduque, F. Aguilera, F.J. Lahoz, J.A. López, L.A. Oro,

M.T. Pinillos, Inorg. Chim. Acta 274 (1983) 15;
(e) C. Tejel, B.E. Villarroya, M.A. Ciriano, A.J. Edwards, F.J. Lahoz, L.A. Oro, M. Lanfranchi, A. Tiripicchio, M. Tiripicchio-Camellini, Inorg. Chem. 37 (1998) 3954.

[5] (a) D.L. Jameson, L.E. Guise, Tetrahedron Lett. 32 (1991) 1999;
(b) A.J. Amoroso, A.M.C. Thompson, J.C. Jeffery, P.L. Jones, J.A. McCleverty, M.D. Ward, J. Chem. Soc., Chem. Commun. (1994) 2751;
(c) F. Al-Omran, N. Al-Awadi, A.A. El-Khair, M.H. Elnagdi, Org. Prep. Proced. 29 (1997) 285;
(d) H. Brunner, T. Scheck, Chem. Ber. 125 (1992) 701;
(e) F. Wang, A.W. Schwabacher, Tetrahedron Lett. 40 (1999) 4779.

[6] (a) J.P. Collman, L.S. Hedeus, J.R. Norton, R.A. Finke, Principles and Applications of Organotransition Metal Chemistry, 2nd ed., University Science Books, Mill Valley, CA, 1987, p. 279;
(b) J.D. Atwood, Inorganic and Organometallic Reaction Mecanisms, 2nd ed., VCH, New York, p. 149;
(c) L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.

[7] (a) P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian, J. Fischer, A. Tiripicchio, F. Ugozzoli, Organometallics 15 (1996) 5551;
(b) J.M. Casas, L.R. Falvello, J. Forniés, A. Martín, Inorg. Chem. 35 (1996) 56;
(c) B. Müller, A. Schneider, M. Tesmer, H. Vahrenkamp, Inorg. Chem. 38 (1999) 1900.

[8] J. Browning, P.L. Goggin, R.J. Goodfellow, M.G. Norton, A.J.M. Rattray, B.F. Taylor, J. Mink, J. Chem. Soc., Dalton Trans. (1977) 2061.

[9] (a) L.A. Oro, M.J. Fernandez, J. Modrego, J.M. López, J. Organomet. Chem. 287 (1985) 409;
(b) A. Elduque, F. Aguilera, F.J. Lahoz, J.A. López, L.A. Oro, M.T. Pinillos, Inorg. Chim. Acta 274 (1998) 15;
(c) A. Elduque, Y. Garcés, L.A. Oro, M.T. Pinillos, A. Tirippicchio, F. Ugozzoli, J. Chem. Soc., Dalton Trans. (1996) 2155.

[10] (a) E. Anzuela, M.A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M.A. Monge, Inorg. Chim. Acta 185 (1991) 211;
(b) G. Tresoldi, P. Piriano, E. Rotondo, F. Faraone, J. Chem. Soc., Dalton Trans. (1991) 425;
(c) S.J. Chadwell, S.J. Coles, P.G. Edwards, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1996) 1105;
(d) B. Crociani, F. Di Bianca, M. Paci, T. Boschi, Inorg. Chim. Acta 145 (1988) 253.

[11] A.P. Martínez, M.P. García, F.J. Lahoz, L.A. Oro, Inorg. Chem. Commun 3 (2002) 245.

[12] (a) L.M. Vallarino, Inorg. Chem. 4 (1965) 161;
(b) P.S. Braterman, Metal Carbonyl Spectra, Academic Press, London, 1975.

[13] A. Bondi, J. Phys. Chem. 68 (1964) 441.

[14] G. Aullón, D. Bellamy, L. Brammer, E.A. Bruton, A.G. Orpen, Chem. Commun. (1998) 653.

[15] (a) S. Bahattacharya, C.G. Pierpoint, Inorg. Chem. 31 (1992) 2020;
(b) J. Charalambous, W.C. Stoten, K. Henrik, Polyhedron 8 (1989) 103.

[16] F.H. Allen, O. Kennard, Chem. Des. Automation News 8 (1993) 1.

[17] E. Bejan, H. Aït Haddou, J.C. Daran, G.G.A. Balavoine, Synthesis (1996) 1012.

[18] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. (1987) S1.

[19] (a) M.A. Garralda, R. Hernandez, L. Ibarlucea, M.I. Arriortua, M.K. Urtiaga, Inorg. Chim. Acta 232 (1995) 9;
(b) G. Vasapollo, A. Sacco, C.F. Nobile, M.A. Pellinghelli, M. Lanfranchi, J. Organomet. Chem. 312 (1986) 249;
(c) M.C. Bonnet, I. Tkatchenko, R. Faure, H. Loiseleur, Nouv. J. Chim. 7 (1983) 601;
(d) M.A. Esteruelas, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, R.M. Claramunt, C. Lopez, J. Elguero, M. Begtrup, J. Organomet. Chem. 344 (1988) 93.

[20] D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969.

[21] G. Giordano, R.H. Crabtree, Inorg. Synth. 19 (1979) 248.

[22] Z. Nagy, S. Vastag, B. Heil, L. Markó, J. Organomet. Chem. 171 (1979) 97.

[23] J.L. Herde, J.C. Lambert, C.V. Senoff, Inorg. Synth. 15 (1974) 18.

[24] R. Usón, L.A. Oro, J.A. Cabeza, Inorg. Synth. 23 (1985) 126.

[25] C.G. Pitt, L.K. Monteith, L.F. Ballard, J.P. Collman, J.C. Morrow, W.R. Roper, D. Ulk, J. Am. Chem. Soc. 88 (1966) 4286.

[26] R. Usón, L.A. Oro, D. Carmona, M.A. Esteruelas, J. Organomet. Chem. 254 (1983) 249.

[27] J. Powell, B.L. Shaw, J. Chem. Soc. A (1968) 211.

[28] SMART and SAINT+ Software for CCD Diffractometers, Bruker AXS, Madison, WI, 2000.

[29] G.M. Sheldrick, SADABS, Program for Corrections of Area Detector Data, University of Göttingen, Göttingen, Germany, 1999.

[30] G.M. Sheldrick, SHELXL-97 Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.