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Iridium and rhodium complexes with tetrafluorobenzobarrelene diolefins

Miguel A. Esteruelas, Luis A. Oro *

Department of Inorganic Chemistry, ICMA, University of Zaragoza-CSIC, E-50009 Zaragoza, Spain

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* Corresponding author. Tel.: +34-976-761148; fax: +34-976-761143.
E-mail address: oro@posta.unizar.es (L.A. Oro)

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Abstract

Iridium and rhodium complexes with tetrafluorobenzobarrelene (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene) type diolefins are reviewed. The synthesis of these tetrafluorobenzobarrelene compounds has promoted the development of a rich chemistry, including catalysis, of neutral and cationic, mono- and polynuclear complexes containing the iridium or rhodium–tetrafluorobenzobarrelene moieties, which show significant differences with respect to the chemistry of usual diolefins.

Keywords: Iridium; Rhodium; Diolefin; Tetrafluorobenzobarrelene; Catalysis

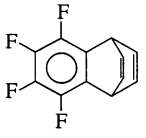
1. Introduction

The ready accessibility of the dinuclear diolefin rhodium and iridium complexes $[M(\mu\text{-}Cl)(COD)]_2$ (M = Rh [1], Ir [2]), $[Rh(\mu\text{-}Cl)(NBD)]_2$ [3] and $[M(\mu\text{-}OMe)(COD)]_2$ (M = Rh, Ir) [4] has promoted the development of an extensive chemistry [5–7] of neutral and cationic complexes containing the rhodium-1,5-cy-

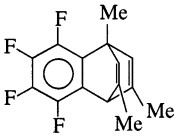
clooctadiene (Rh–COD), rhodium-2,5-norbornadiene (Rh–NBD) and iridium-1,5-cyclooctadiene (Ir–COD) moieties. Related rhodium and iridium diolefin precursors, with conjugated and non-conjugated diolefins have been less extensively used due to their limited accessibility [5–7]. The solid fluorinated barrelene diolefins are unusual but interesting and useful ligands. In particular, the synthesis of tetrafluorobenzobarrelene (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene), initially reported by Massey and coworkers [8,9] is relatively easy. It can be prepared by simple addition of butyllithium to a benzene solution of bromopentafluorobenzene [8]. Thus, the decomposition of the formed pentafluorophenyllithium in the presence of benzene produces tetrafluorobenzobarrelene, as a white solid, which can be purified by sublimation. The related tri- and tetra-methyltetrafluorobenzobarrelene diolefins (Me_3TFB and Me_4TFB) are obtained when the corresponding methyl-substituted benzenes are used (Fig. 1) [9]. A detailed ^{1}H and ^{13}C NMR spectroscopy study of the tetrafluorobenzobarrelene diolefin has been reported [10].

The coordination chemistry of the tetrafluorobenzobarrelene diolefin towards rhodium and iridium should present some special characteristics due to the influence of the electron-withdrawing tetrafluorobarrelene group and, particularly, its smaller bite angle. Interestingly, tetrafluorobenzobarrelene ligands exhibit, in comparison with the usual cyclooctadiene and norbornadiene diolefins, stronger IR absorptions allowing unequivocal assignment and, in addition, the well known tendency towards the formation of oils of the other diolefins is greatly reduced. It is also noteworthy to point out that the tetrafluorobenzobarrelene ligands significantly favour the isolation of crystals suitable for X-ray diffraction studies. In addition to the relatively large number of iridium and rhodium complexes, same osmium and ruthenium complexes with tetrafluorobenzobarrelene ligands have been reported [11,12].

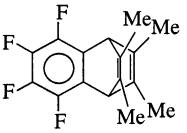
This review will deal with the iridium and rhodium chemistry of fluorinated barrelene diolefins, namely tetrafluorobenzobarrelene (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene) (TFB) and tri- and tetra-methyltetrafluorobenzobarrelene (Me_xTFB, $x = 3$, 4), with particular emphasis on the distinctive differences to other diolefins. At this point it is interesting to note that the reported iridium–tetrafluorobenzobarrelene chemistry presents some interesting novelties in comparison with the iridium chemistry of more conventional diolefins such as 1,5-cycloctadiene. In contrast, the chemistry of rhodium with different diolefins shows more similarities, although in some cases the tetrafluorobenzobarrelene



TFB



Me_3TFB



Me_4TFB

Fig. 1.

ligands have played a significant role for the complete characterisation of some unusual complexes.

2. Iridium tetrafluorobenzobarrelene chemistry

2.1. The starting materials for iridium–diolefin chemistry

Iridium–diolefin chemistry has been traditionally dominated by the iridium-1,5-cyclooctadiene (Ir–COD) unit [7], due to the accessibility to the complex $[Ir(\mu\text{-}Cl)(COD)]_2$. This compound is prepared in high yield by direct reaction of $IrCl_3 \cdot H_2O$ or $[NH_4]_2[IrCl_6]$ with an excess of 1,5-cyclooctadiene in ethanol–water, under reflux [2]. A new synthesis of this precursor using microwave heating for 45 s provided a 72% yield [13].

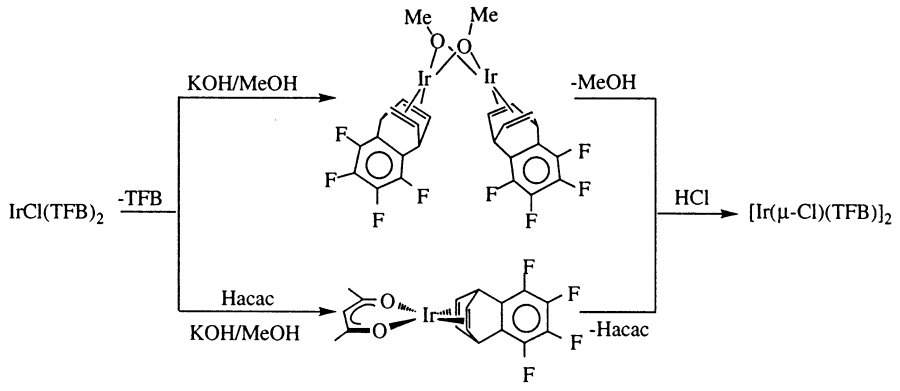
The dimeric complex $[Ir(\mu\text{-}Cl)(COD)]_2$ is also the entry to the chemistry of the iridium–dibenzo[a,e]cyclooctatetraene (Ir–DCT) unit. Thus, it reacts with this diolefin to give $[Ir(\mu\text{-}Cl)(DCT)]_2$. The dibenzo[a,e]cyclooctatetraene diolefin is different from 1,5-cyclooctadiene in several respects: (i) it is substantially more electron-withdrawing; (ii) it is hydrogenation resistant; and (iii) it is more tightly bound [14].

Attempts to obtain a related $[Ir(\mu\text{-}Cl)(NBD)]_2$ (NBD = 2,5-norbornadiene) dimer have been unsuccessful. The reaction of 2,5-norbornadiene with $[Ir(\mu\text{-}Cl)(COD)]_2$ or $[Ir(\mu\text{-}Cl)(cyclooctene)_2]_2$ yields a product containing three norbornadiene units $[IrCl(C_7H_8)_3)]_x$. Treatment of this product with PMe_3 or acetylacetonato affords species containing two of these norbornadiene units half-linked together with *exo–trans–exo* stereochemistry in a five-membered metallacycle, as confirmed by a single-crystal X-ray diffraction study on the complex $Ir(C_{14}H_{16})(acac)(NBD)$ [15].

The mass spectra of the complex $[IrCl(C_7H_8)_3]_x$ is of some interest. It shows no parent peak corresponding to $[IrCl(NBD)_3]^+$ or any multiple of these, the highest m/e isotopic cluster corresponds to the fragment $[IrCl(NBD)]_2^+$ with a relative intensity of 4.6. In addition, a peak of high relative abundance (42.2) appears at m/e 184, corresponding to an NBD-dimer liberated from the iridocycle species [15a].

In contrast to 2,5-norbornadiene, the diolefin tetrafluorobenzabarrelene reacts with the dimer $[Ir(\mu\text{-}Cl)(cyclooctene)_2]_2$ to give $IrCl(TFB)_2$, which can also be prepared in nearly quantitative yield by direct reaction of $IrCl_3 \cdot H_2O$ or $[NH_4]_2[IrCl_6]$ with an excess of diolefin, in ethanol–water under reflux [16]. The related complex $IrCl(COD)_2$ is also known, but in solution, it dissociates and dimerizes to form $[Ir(\mu\text{-}Cl)(COD)]_2$ [17].

Although the complex $IrCl(TFB)_2$ is not readily soluble, it allows the preparation of the dimer $[Ir(\mu\text{-}Cl)(TFB)]_2$ via the two routes shown in Scheme 1. Treatment of methanol suspensions of $IrCl(TFB)_2$ with potassium hydroxide affords the dimer $[Ir(\mu\text{-}OMe)(TFB)]_2$, whereas under the same conditions, but in the presence of acetylacetone, the acetylacetonato compound Ir(acac)(TFB) is obtained. Both derivatives react with hydrochloric acid to give the dinuclear species $[Ir(\mu\text{-}Cl)(TFB)]_2$. The dinuclear complex $[Ir(\mu\text{-}Cl)(Me_3TFB)]_2$ containing the trimethyltetrafluorobenzobarrelene diolefin is prepared similarly to $[Ir(\mu\text{-}Cl)(COD)]_2$, by direct reaction of $IrCl_3 \cdot H_2O$ with an excess of the diolefin in ethanol–water under reflux [18].



Scheme 1.

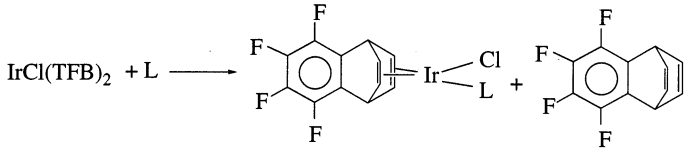
The discovery of these tetrafluorobenzobarrelene compounds has promoted the development of a rich chemistry, including catalysis, of neutral and cationic complexes containing the iridium–tetrafluorobenzobarrelene moiety, which shows significant differences with respect to the chemistry of the typical iridium-1,5-cyclooctadiene moiety. This development has been marked by the particular characteristics of the starting material $IrCl(TFB)_2$ and by the fact that complexes Ir(acac)(TFB) and $[Ir(\mu\text{-}OMe)(TFB)]_2$ are precursors for the dimer $[Ir(\mu\text{-}Cl)(TFB)]_2$. Thus, three ways of expansion can be clearly pointed out, corresponding to the use of the complexes $IrCl(TFB)_2$, Ir(acac)(TFB) and $[Ir(\mu\text{-}OMe)(TFB)]_2$ as starting materials.

2.2. The complex $IrCl(TFB)_2$ as a precursor for neutral compounds

The five-coordinate complex $IrCl(TFB)_2$ is a useful starting material to prepare square–planar iridium(I) complexes which, by oxidative addition, afford six-coordinate hydrido–iridium(III) derivatives. In addition, the use of bidentate P- or N-donor ligands as well as $AsPh_3$ and $SbPh_3$ has led to the formation of five-coordinate iridium(I) compounds.

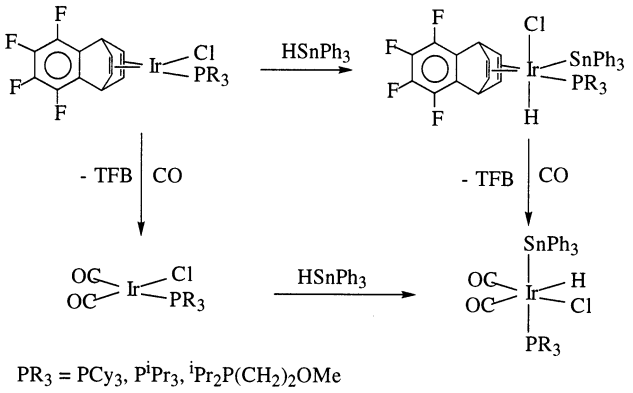
2.2.1. Square–planar iridium(I) and six-coordinate iridium(III) complexes

Complex $IrCl(TFB)_2$ reacts with an excess of 2-methylpyridine (2-Mepy), quinoline (quin) and pyrazole (Hpz), and with a stoichiometric amount of phosphine to give square–planar compounds of the type IrCl(TFB)L [19–22], according to Eq. 1:



(1)

L = 2-Mepy, quin, Hpz, PPh_3, PCy_3, P^iPr_3, $^iPr_2P(CH_2)_2OMe$.



Scheme 2.

Treatment of toluene or chloroform solutions of $IrCl(TFB)(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3, $^iPr_2P(CH_2)_2(OMe)$) with ca. 1 equiv. of $HSnPh_3$ leads immediately to the formation of the corresponding hydrido-complexes $IrH(SnPh_3)Cl(TFB)(PR_3)$ (Scheme 2) [21]. Since the oxidative addition of stannanes, as well as the oxidative addition of silanes and molecular hydrogen, to square–planar iridium(I) complexes seems to be a concerted *cis*-addition process [23], the stereochemistry of $IrH(SnPh_3)Cl(TFB)(PR_3)$ with the hydrido and stannyl group *trans* disposed to the chlorine and diene, respectively, suggests that the addition of $HSnPh_3$ to the square–planar starting materials occurs by approach of the substrate along the olefin–Ir–Cl axis, with the tin atom above the chlorine atom (Fig. 2).

The tetrafluorobenzobarrelene diolefin of $IrCl(TFB)(PR_3)$ can be displaced by carbon monoxide to afford the *cis*-dicarbonyl derivatives $IrCl(CO)_2(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3, $^iPr_2P(CH_2)_2OMe$), which react with $HSnPh_3$ to give $IrH(SnPh_3)Cl(CO)_2(PR_3)$. The stereochemistry of these compounds (see Scheme 2) suggests that, in this case, the addition of the stannane occurs along the OC–Ir–P axis, with the tin atom above the carbonyl group (Fig. 3).

The complexes $IrH(SnPh_3)Cl(CO)_2(PR_3)$ are also obtained in high yield (about 80%) by reaction of $IrH(SnPh_3)Cl(TFB)(PR_3)$ with carbon monoxide suggesting that, in these *cis*-dicarbonyl iridium(III) compounds, the disposition of the stannyl group is thermodynamically favoured.

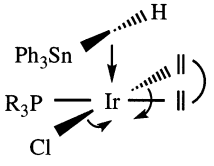


Fig. 2.

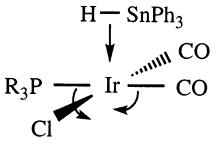
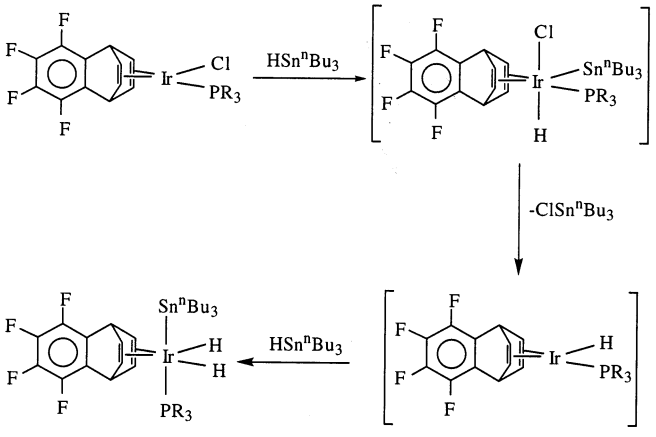


Fig. 3.

The complexes IrCl(TFB)(PR_3) ($PR_3 = PCy_3$, P^iPr_3) also react with HSn^nBu_3. However, in contrast to the addition of $HSnPh_3$, the reactions lead to the dihydridostannyl derivatives $IrH_2(Sn^nBu_3)(TFB)(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3) [21]. When the reactions are carried out in a 1:1 molar ratio, mixtures of the starting materials and the dihydrido products are obtained. The quantitative formation of $IrH_2(Sn^nBu_3)(TFB)(PR_3)$, determined by NMR spectroscopy, only occurs when 2 equiv. of HSn^nBu_3 are added. The formation of $IrH_2(Sn^nBu_3)(TFB)(PR_3)$ most probably involves the oxidative addition of the stannane to the starting materials to give $IrH(Sn^nBu_3)Cl(TFB)(PR_3)$ intermediates similar to $IrH(SnPh_3)Cl(TFB)(PR_3)$. The subsequent elimination of $ClSn^nBu_3$ followed by the oxidative addition of a second stannane molecule to $IrH(TFB)(PR_3)$ intermediates should afford $IrH_2(Sn^nBu_3)(TFB)(PR_3)$ (Scheme 3).

On treatment with AgOTf, the chloro-complexes IrCl(TFB)(PR_3) give the square planar derivatives Ir(OTf)(TFB)(PR_3) ($PR_3 = PCy_3$, P^iPr_3) [20] (Scheme 4). The reactions of these compounds with 1 equiv. of $HSnPh_3$ in toluene at room temperature (r.t.) afford the corresponding $IrH(SnPh_3)(OTf)(TFB)(PR_3)$ [21], containing the stannyl group *trans* to the phosphine ligand. This geometry suggests that, in contrast to the oxidative addition of $HSnPh_3$ to IrCl(TFB)(PR_3), the reactions of Ir(OTf)(TFB)(PR_3) with $HSnPh_3$ take place along the olefin–Ir–P axis, with the tin atom above one of the two olefinic bonds of the diene (Fig. 4).



Scheme 3.

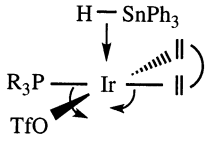
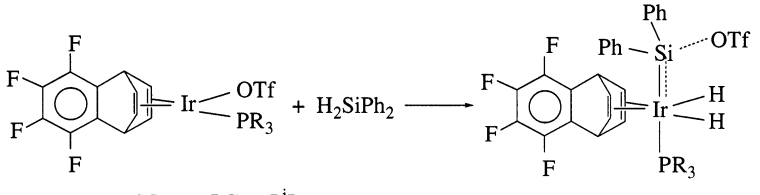


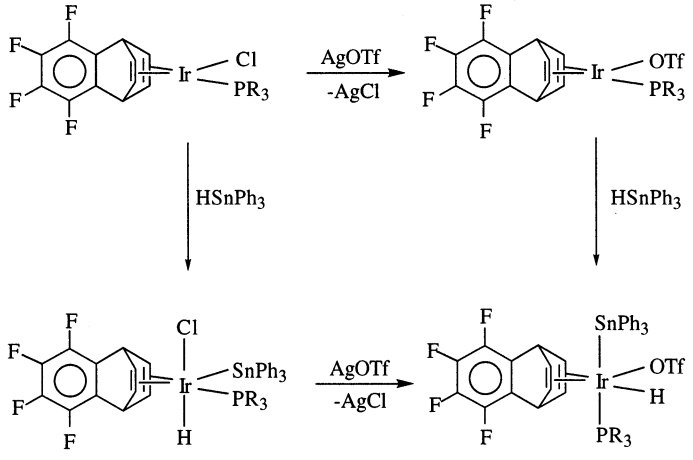
Fig. 4.

The approach shown in Fig. 4 appears to be kinetically favoured and the stereochemistry shown in Scheme 4 also seems to be thermodynamically favoured. In agreement with this, the complexes $IrH(SnPh_3)(OTf)(TFB)(PR_3)$ are also obtained by reaction of $IrH(SnPh_3)Cl(TFB)(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3) with AgOTf.

The complexes $Ir(OTf)(TFB)(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3) also react with H_2SiPh_2. However, in this case, the reaction products are the base-stabilised silylene derivatives $IrH_2\{Si(OTf)Ph_2\}(TFB)(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3) (Eq. 2) [20]. The silylene character of the $Si(OTf)Ph_2$ ligand has been established by an X-ray investigation on a single crystal of $IrH_2\{Si(OTf)Ph_2\}(TFB)(P^iPr_3)$.

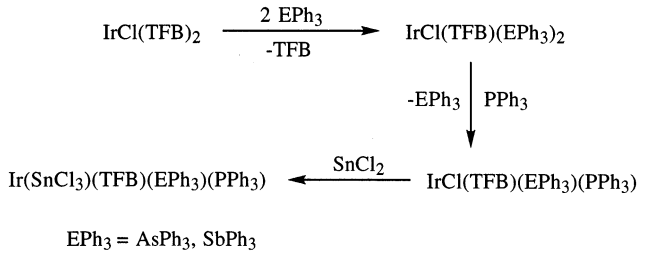


PR_3 = PCy_3, P^iPr_3. (2)



$PR_3 = PCy_3$, P^iPr_3

Scheme 4.



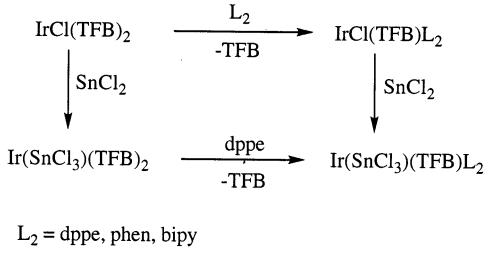
Scheme 5.

The formation of these compounds probably involves the initial oxidative addition of H_2SiPh_2 to Ir(OTf)(TFB)(PR_3) to give hydrido–silyl intermediates of the type IrH($SiHPh_2$)(OTf)(TFB)(PR_3). The dissociation of the phosphine ligands from these intermediates should lead to the unsaturated species IrH($SiHPh_2$)(OTf)-(TFB) which, by an α-elimination reaction, should give the silylene derivative IrH_2(=$SiPh_2$)(OTf)(TFB). Subsequent attack of the $[OTf]^-$ anion at the silylene group could afford the unsaturated dihydrido IrH_2{Si(OTf)Ph_2}(TFB) which, by coordination of the phosphine ligand, should give IrH_2{Si(OTf)Ph_2}(TFB)-(PR_3).

2.2.2. Five coordinate iridium(I) complexes

The treatment of acetone suspensions of $IrCl(TFB)_2$ with 2 equiv. of triphenylarsine and triphenylstibine produces the displacement of a coordinated tetrafluorobenzobarrelene ligand and the formation of IrCl(TFB)(EPh_3)$_2$ (EPh_3 = $AsPh_3$, $SbPh_3$) [19]. These compounds react with triphenylphosphine to give mixed complexes of general formula IrCl(TFB)(EPh_3)(PPh_3) (Scheme 5), which can also be obtained by addition of triphenylarsine or triphenylstibine to IrCl(TFB)(PPh_3). Similarly, the addition of triphenylphosphine to IrCl(TFB)(PPh_3) affords the five-coordinate derivative IrCl(TFB)(PPh_3)$_2$.

Five-coordinate compounds of the type IrCl(TFB)L_2, containing bidentate ligands such as bis(1,2-diphenylphospine)ethane (dppe), 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy), are prepared similarly to IrCl(TFB)(EPh_3)$_2$, by addition of the stoichiometric amount of the bidentate ligand to the acetone suspensions of



Scheme 6.

$IrCl(TFB)_2$ (Scheme 6). The reaction of $IrCl(TFB)_2$ with tris(pyrazol-1-yl)methane (tpzm) leads to IrCl(TFB)(tpzm) [24].

Refluxing an ethanol suspension of $IrCl(TFB)_2$ with $SnCl_2{\cdot}2H_2O$ during three days gives rise to the formation of $Ir(SnCl_3)(TFB)_2$ in 80% yield. The resulting complex reacts slowly with PPh_3 to form $Ir(SnCl_3)(TFB)(PPh_3)_2$. By contrast, one molecule of 1,5-cyclooctadiene is promptly displaced in the related $Ir(SnCl_3)(COD)_2$ [25a]. A more appropriate preparative route to obtain five-coordinate trichlorotin complexes is the addition of $SnCl_2{\cdot}2H_2O$ to acetone solutions of $IrCl(TFB)(EPh_3)_2$ (Eq. (3)) or $IrCl(TFB)L_2$ (Scheme 6):

$$IrCl(TFB)(EPh_3)_2 + SnCl_2 \rightarrow Ir(SnCl_3)(TFB)(EPh_3)_2 \quad (3)$$

$EPh_3 = AsPh_3$, $SbPh_3$.

In acetone, the mixed complexes $IrCl(TFB)(EPh_3)(PPh_3)$ do not react with $SnCl_2{\cdot}2H_2O$. However, in methanol, which favours the formation of the ionic pair $[Ir(TFB)(EPh_3)(PPh_3)]^+Cl^-$, the addition of $SnCl_2{\cdot}2H_2O$ leads to the instantaneous precipitation of $Ir(SnCl_3)(TFB)(EPh_3)(PPh_3)$ (Scheme 5).

Molar conductivity measurements and osmometrical determinations [25b–d] indicate that the five-coordinate iridium(I)–tetrafluorobenzobarrelene compounds have a lower tendency to dissociate a ligand from the coordination sphere of the metal than the related five-coordinate iridium(I)-1,5-cyclooctadiene compounds.

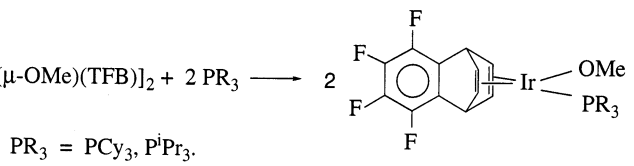
The higher tendency of the Ir–TFB unit to stabilise five-coordinate species is also revealed by the reaction of $IrCl(TFB)_2$ with $AgClO_4$, which leads to the covalent perchlorate complex $Ir(OClO_3)(TFB)_2$ [19], whilst the related compound in the 1,5-cyclooctadiene chemistry, $[Ir(COD)_2]ClO_4$, is a four-coordinate species [26].

2.3. The dimer [Ir(μ-OMe)(TFB)]$_2$ as a precursor for neutral compounds

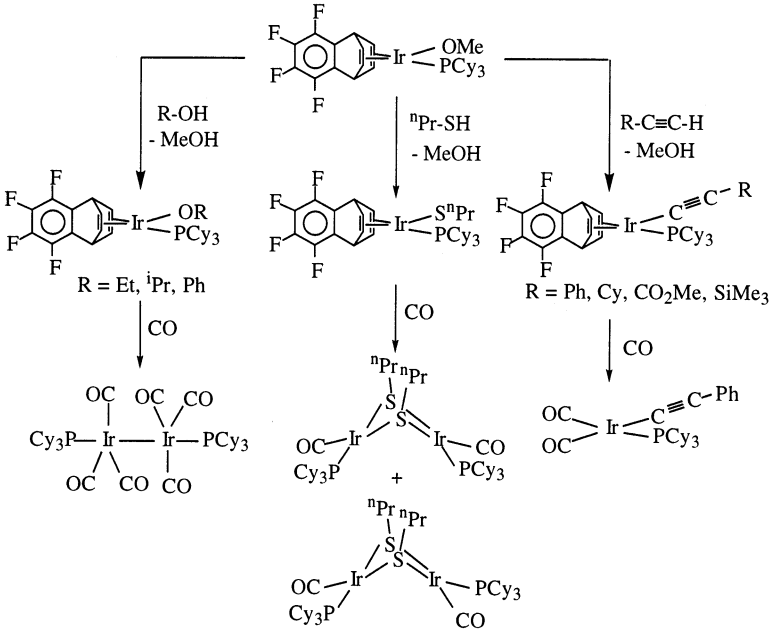
Complex $[Ir(\mu\text{-OMe})(TFB)]_2$ has been a key compound in the development of the chemistry of the Ir–TFB unit. As a result of its reactions with bulky phosphines, a variety of unusual $Ir(XR)(TFB)(PR_3)$ compounds have been synthesised, which have subsequently given rise to interesting iridium(III) derivatives via oxidative addition reactions. In addition, the methoxide group has shown to be a very good leaving group, and thus, the reactions of the complex $[Ir(\mu\text{-OMe})(TFB)]_2$ with molecules containing relatively acidic protons have led to new families of homodinuclear and heterodinuclear derivatives.

2.3.1. Mononuclear Ir(XR)(TFB)(PR$_3$) complexes

Complex $[Ir(\mu\text{-OMe})(TFB)]_2$ reacts with bulky phosphines such as PCy_3 and P^iPr_3 to afford square–planar complexes of the type $Ir(OMe)(TFB)(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3), according to Eq. 4 [27]:



(4)



Scheme 7.

In contrast to these bulky phosphines, the addition of the smaller PPh_3, and the diphosphines dppe and dppp (bis(1,3-diphenylphosphino)propane), to methanol suspensions of $[Ir(\mu\text{-}OMe)(TFB)]_2$ leads to the five-coordinate complexes $IrH(TFB)L_2$, according to Eq. (5). The related compound $IrH(TFB)(AsPh_3)_2$ is prepared by reaction of $IrCl(TFB)(AsPh_3)_2$ with a methanolic solution of potassium hydroxide [28]:

$$[Ir(\mu\text{-}OMe)(TFB)]_2 + 2L_2 \rightarrow 2IrH(TFB)L_2 + 2H_2CO \quad (5)$$

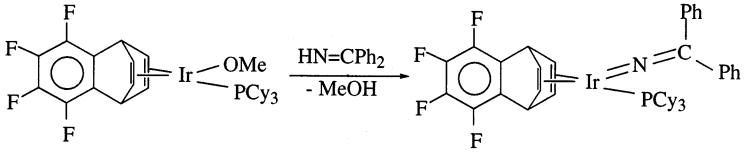
$L = PPh_3$; $L_2 =$ dppe, dppp.

In the presence of ethanol, 2-propanol or phenol, the tricyclohexylphosphine complex $Ir(OMe)(TFB)(PCy_3)$ exchanges the alkoxy group to give the derivatives $Ir(OR)(TFB)(PCy_3)$ shown in Scheme 7, [29]. Related alkoxide compounds of the Vaska type are prepared by metathesis of the chloride ligands [30]. Under carbon monoxide atmosphere both $Ir(OR)(TFB)(PCy_3)$ and *trans*-$Ir(OR)(CO)(PR_3)_2$ afford the corresponding hexacarbonyl derivatives $Ir_2(CO)_6(PR_3)_2$ [29,31].

The complex $Ir(OMe)(TFB)(PCy_3)$ also reacts with propanethiol and terminal alkynes (Scheme 7). The reaction with propanethiol leads to the thiopropoxide $Ir(S^nPr)(TFB)(PCy_3)$, which, under carbon monoxide atmosphere, affords the dinuclear dicarbonyl compound $[Ir(\mu\text{-}S^nPr)(CO)(PCy_3)]_2$, isolated as a mixture of *cis* and *trans* isomers in a 7:3 molar ratio. The formation of these isomers has been monitored by IR spectroscopy in dichloromethane solution and appears to proceed

via the *cis*-dicarbonyl intermediate $Ir(S^nPr)(CO)_2(PCy_3)$ which, by loss of a carbon monoxide molecule, affords $[Ir(\mu\text{-}S^nPr)(CO)(PCy_3)]_2$. Treatment of Ir(OMe)-(TFB)(PCy_3) with a stoichiometric amount of phenylacetylene, cyclohexylacetylene, methylpropiolate or trimethylsilyl acetylene yields the corresponding alkynyl derivatives $Ir(C_2R)(TFB)(PCy_3)$. The tetrafluorobenzobarrelene diolefin of $Ir(C_2Ph)(TFB)(PCy_3)$ can be displaced by carbon monoxide to give *cis*-$Ir(C_2Ph)(CO)_2(PCy_3)_2$ which, in contrast to *cis*-$Ir(S^nPr)(CO)_2(PCy_3)$, is stable and does not evolve into a dinuclear compound containing bridging alkynyl ligands [29].

Complex Ir(OMe)(TFB)(PCy_3) and the related 1,5-cyclooctadiene Ir(OMe)-(COD)(PCy_3) are precursors for the only known neutral iridium–azavinylidenes. These compounds, $Ir(=N=CPh_2)(diene)(PR_3)$ (diene = TFB, COD), are obtained by reaction of Ir(OMe)(diene)(PCy_3) (diene = TFB, COD) with benzophenone imine, as shown in Eq. 6 for the tetrafluorobenzobarrelene derivative.



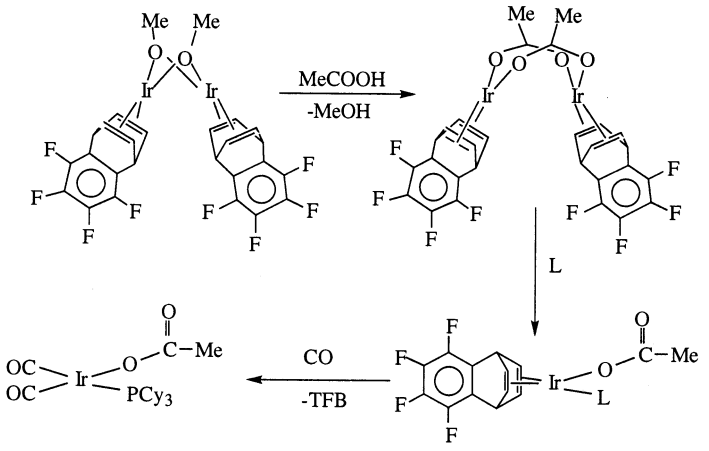
(6)

From a spectroscopic point of view, it should be mentioned that the resonance due to the olefinic carbon atoms *trans* to the azavinylidene ligand appears at an unusually high field (16.15 ppm) in the $^{13}C\{^1H\}$ NMR spectrum of $Ir(=N=CPh_2)(TFB)(PCy_3)$ [27a]. This is in agreement with the stronger π-donor ability of the azavinylidene groups, which are generally viewed as three-electron donor ligands [32].

2.3.2. Hydrido–silyl complexes [33]

Another interesting compound, which has also helped to develop the chemistry of the Ir–TFB unit, is the diacetato–dimer $[Ir(\mu\text{-}O_2CCH_3)(TFB)]_2$. This complex can be obtained in 80% yield, by reaction of $[Ir(\mu\text{-}OMe)(TFB)]_2$ with acetic acid in acetone/2-propanol (1:5) [33]. The acetato bridges of this complex are readily split by monodentate ligands such as pyridine or phosphines to give the square–planar derivatives $Ir\{\kappa^1\text{-}OC(O)Me\}(TFB)L$ (L = py, PPh_3, PCy_3, P^iPr_3). The tetrafluorobenzobarrelene diolefin of the tricyclohexylphosphine complex $Ir\{\kappa^1\text{-}OC(O)Me\}(TFB)(PCy_3)$ can be displaced by carbon monoxide to afford $Ir\{\kappa^1\text{-}OC(O)Me\}(CO)_2(PCy_3)$ (Scheme 8), which undergoes further reactions with $HSnPh_3$ or $HSiR_3$ ($HSiR_3$ = $HSiPh_3$, $HSiEt_3$, H_2SiPh_2 or H_3SiPh) to give dihydrido stannyl, bis(stannyl), dihydrido silyl and bis(silyl) derivatives, depending upon the nature of the reagent used [34].

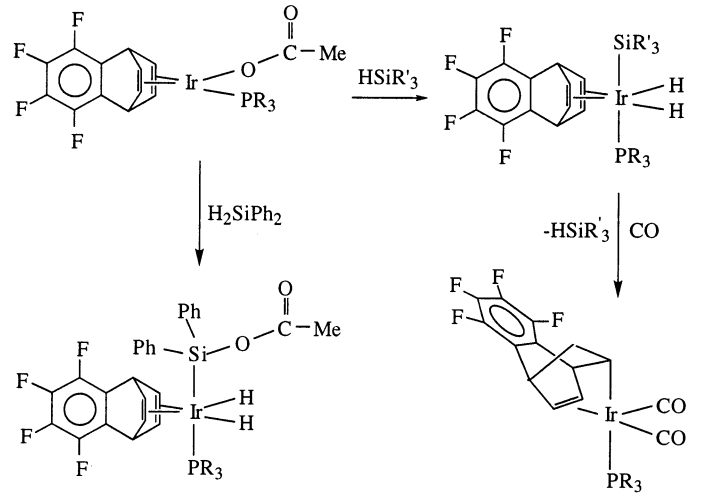
The complexes $Ir\{\kappa^1\text{-}OC(O)Me\}(TFB)(PR_3)$ (PR_3 = PPh_3, PCy_3, P^iPr_3) react with $HSiEt_3$ or $HSiPh_3$ to give the corresponding dihydrido–silyl derivatives $IrH_2(SiR'_3)(TFB)(PR_3)$ [33]. The related 1,5-cyclooctadiene compounds $IrH_2(SiR_3)(COD)(PPh_3)$, $IrH_2(SiR_3)(COD)(AsPh_3)$ [35] and $IrH_2(SiR_3)$-(COD)(PCy_3) [36] (SiR_3 = $SiEt_3$ or $SiMe_2Ph$) are prepared by reaction of



Scheme 8.

the dimer $[Ir(\mu\text{-}OMe)(COD)]_2$ with $HSiR_3$ in the presence of the corresponding phosphine or arsine. In the absence of these ligands a $Ir_2H_2(C_6H_4SiMe_2)_4$ dimer is obtained [37].

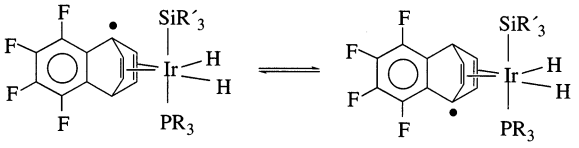
The disposition of the ligands around the iridium atom of $IrH_2(SiR'_3)(TFB)(PR_3)$ (see Scheme 9) leads to a situation where the aliphatic CH protons of the tetrafluorobenzobarrelene diolefin are chemically inequivalent; furthermore, the



Scheme 9.

protons of each carbon–carbon double bond are also mutually inequivalent although both olefinic bonds are chemically equivalent. In agreement with this, the ^{1}H NMR spectra of these compounds display two aliphatic and two olefinic signals at -55°C. However, at r.t. the spectra do not contain resonances due to the diolefin, or show two resonances, one due to the aliphatic protons and the other to the olefinic protons. In order to rationalise this behaviour, it has been proposed that $IrH_2(SiR'_3)(TFB)(PR_3)$ only has a rigid structure at low temperature.

At r.t. an intramolecular exchange process takes place involving the relative positions of the atoms of the diolefin (Eq. 7):



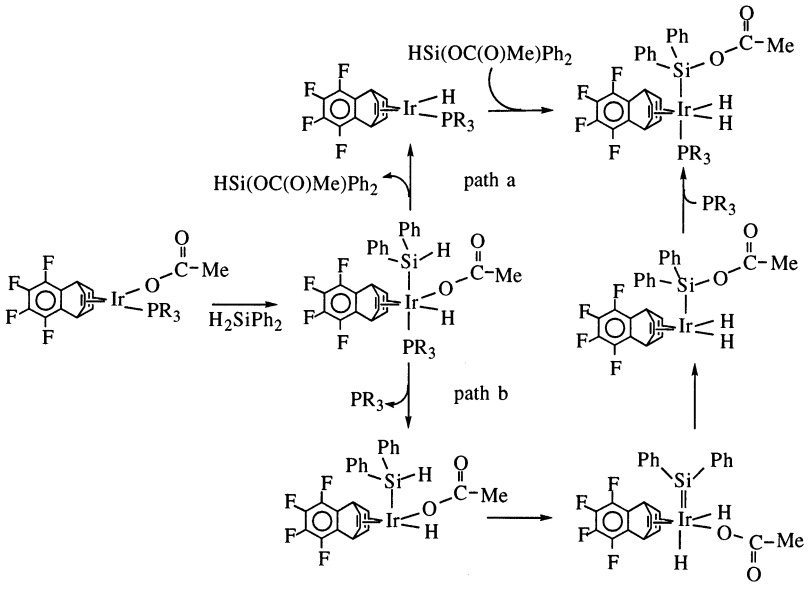
(7)

This fluxional process could proceed via a five-coordinate intermediate of the type, $IrH_2(SiR'_3)(TFB)$, which could be formed by dissociation of the phosphine ligand from $IrH_2(SiR'_3)(TFB)(PR_3)$. In accordance with this proposal, it has been observed that the addition of P^iPr_3 to a benzene solution of $IrH_2(SiEt_3)(TFB)(PCy_3)$ in a 1:1 molar ratio leads to a mixture of $IrH_2(SiEt_3)(TFB)(P^iPr_3)$, $IrH_2(SiEt_3)(TFB)(PCy_3)$, PCy_3 and P^iPr_3 in a 1:1:1:1 molar ratio, after 22 h [33].

The reactions of $IrH_2(SiR'_3)(TFB)(PR_3)$ with carbon monoxide (r.t., 1 atm) induce a reductive elimination of $HSiR'_3$ ($R' = Et$, Ph) and the corresponding formation of $Ir(\eta^1{:}\eta^2\text{-}C_{12}F_4H_7)(CO)_2(PR_3)$ ($PR_3 = PPh_3$, PCy_3, P^iPr_3) where the $\eta^1{:}\eta^2$ – coordination mode of the $C_{12}F_4H_7$ ligand has been established by an X-ray investigation on a monocrystal of the tricyclohexyphosphine derivative.

The complexes $Ir\{\kappa^1\text{-}OC(O)Me\}(TFB)(PR_3)$ ($PR_3 = PPh_3$, PCy_3, P^iPr_3) also react with H_2SiPh_2. These reactions lead to $IrH_2\{Ph_2SiOC(O)Me\}(TFB)(PR_3)$ (Scheme 9), containing an acetoxydiphenylsilyl ligand. Scheme 10 illustrates two plausible reaction routes which allow the formation of these compounds to be rationalised. For both paths, the first step could involve the oxidative addition of H_2SiPh_2 to $Ir\{\kappa^1\text{-}OC(O)Me\}(TFB)(PR_3)$, giving hydrido silyl intermediates of the type $IrH(SiHPh_2)\{\kappa^1\text{-}OC(O)Me\}(TFB)(PR_3)$. Path *a* involves reductive elimination of $HSi\{OC(O)Me\}Ph_2$ and subsequent oxidative addition of $HSi\{OC(O)Me\}Ph_2$ to $IrH(TFB)(PR_3)$. According to path *b*, the dissociation of the phosphine ligand from $IrH(SiHPh_2)\{\kappa^1\text{-}OC(O)Me\}(TFB)((PR_3)$ could lead to the unsaturated species $IrH(SiHPh_2)\{\kappa^1\text{-}OC(O)Me\}(TFB)$ which, by an α-elimination reaction, should give the silylene derivative $IrH_2(=SiPh_2)\{\kappa^1\text{-}OC(O)CH_3\}(TFB)$. The silylene group could then be attacked by the acetato ligand to form the unsaturated dihydrido acetoxydiphenylsilyl intermediate $IrH_2\{Ph_2SiOC(O)Me\}(TFB)$, which, by coordination of the phosphine ligand, should give $IrH_2\{Ph_2SiOC(O)Me\}(TFB)(PR_3)$.

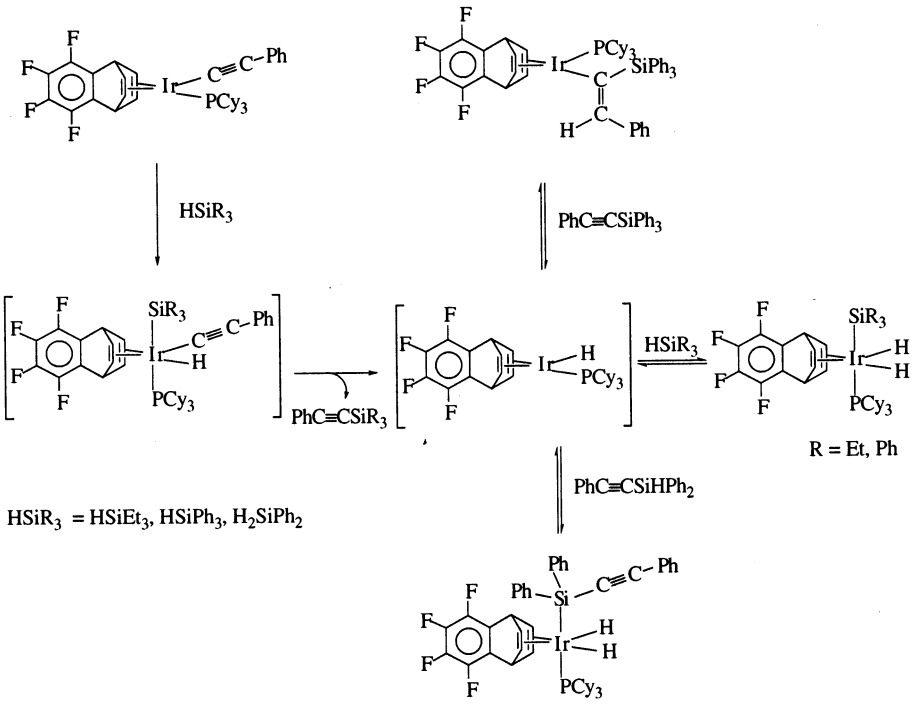
Dihydrido–silyl complexes can also be obtained by reaction of $Ir(C_2Ph)$-$(TFB)(PCy_3)$ with $HSiEt_3$, $HSiPh_3$ or H_2SiPh_2. The reaction products depend upon which silane is used [38].



Scheme 10.

The reaction of $Ir(C_2Ph)(TFB)(PCy_3)$ with one equiv. of $HSiEt_3$ leads to a mixture of $IrH_2(SiEt_3)(TFB)(PCy_3)$, $Ir(C_2Ph)(TFB)(PCy_3)$ and $PhC{\equiv}CSiEt_3$ in a 1:1:1 molar ratio. However, the addition of $HSiEt_3$ to a solution of $Ir(C_2Ph)(TFB)(PCy_3)$ in a 2:1 molar ratio affords, in quantitative yield, $IrH_2(SiEt_3)(TFB)(PCy_3)$ and $PhC{\equiv}CSiEt_3$ in a 1:1 molar ratio. These results has been rationalised according to Scheme 11. In agreement with the oxidative addition of $HSiR_3$ to $Ir(C_2Ph)(CO)_2(PCy_3)$, which gives $IrH(C_2Ph)(SiR_3)(CO)_2(PCy_3)$ ($SiR_3 = SiEt_3$, $SiPh_3$, $SiHPh_2$), it has been proposed that the reaction could initially involve the oxidative addition of $HSiEt_3$ to $Ir(C_2Ph)(TFB)(PCy_3)$, along the olefin–Ir–P axis (Fig. 5) to give $IrH(C_2Ph)(SiEt_3)(TFB)(PCy_3)$, followed by reductive elimination of $Ph{\equiv}CSiEt_3$ to give $IrH(TFB)(PCy_3)$. The subsequent oxidative addition of a second molecule of $HSiEt_3$ to $IrH(TFB)(PCy_3)$ should lead to $IrH_2(SiEt_3)(TFB)(PCy_3)$.

The elimination of $PhC{\equiv}CSiEt_3$ from $IrH(C_2Ph)(SiEt_3)(TFB)(PCy_3)$ is noteworthy. Due to the facial disposition of the silyl, hydrido, and alkynyl ligands in $IrH(C_2Ph)(SiEt_3)(TFB)(PCy_3)$ (see Scheme 11), three unimolecular reductive eliminations are possible, leading to $HSiEt_3$, $PhC{\equiv}CH$ or $PhC{\equiv}CSiEt_3$. The first one is the less interesting because it regenerates $Ir(C_2Ph)(TFB)(PCy_3)$. However, of particular interest is the question of competitive $PhC{\equiv}CH$ vs. $PhC{\equiv}CSiEt_3$ reductive elimination. Whereas the reductive elimination of a C–H bond is a well-documented process [39], there are very few examples for the reductive elimination of Si–C bonds [40]. Milstein et al. [41] have studied the possible reductive elimination from complexes of type *fac*-$IrHMe(SiR_3)(PMe_3)_3$. While both the $Si(OEt)_3$ and $SiPh_3$ derivatives exclusively liberate CH_4 on heating, the $SiEt_3$ derivative gives CH_4



Scheme 11.

and $MeSiEt_3$ in a 4:1 molar ratio. The different behaviours of the SiR_3 complexes have been attributed to the different π-Si–M bond strengths. Electron-donating groups at the silicon atom weaken the π-Si–M bond and make the Si–C elimination competitive with the C–H elimination.

The intermediate $IrH(C_2Ph)(SiEt_3)(TFB)(PCy_3)$ exclusively eliminates $PhC{\equiv}CSiR_3$. The reductive elimination of phenylacetylene does not occur because of the *cis* constraint imposed by the chelating tetrafluorobenzobarrelene ligand and the fact that in a concerted reductive elimination, the ligands *trans* to the leaving ligands move into mutually *trans* positions in the resulting four-coordinate complex. Thus, the 'unfavourable' Si–C elimination becomes the only possible alternative.

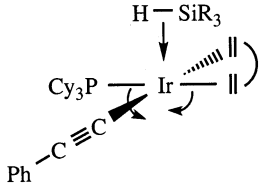


Fig. 5.

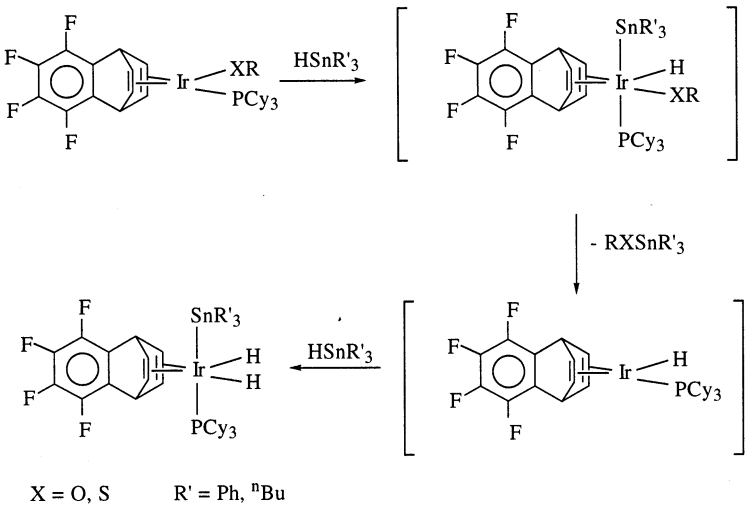
Si–C bonds are also formed from the reactions of $Ir(C_2Ph)(TFB)(PCy_3)$ with $HSiPh_3$ and H_2SiPh_2. The reaction of $Ir(C_2Ph)(TFB)(PCy_3)$ with 1 equiv. of $HSiPh_3$ leads to a mixture of the alkenyl complex $Ir\{C(SiPh_3)=CHPh\}(TFB)(PCy_3)$ (50%) and $IrH_2(SiPh_3)(TFB)(PCy_3)$ (19%). In addition the formation of $PhC\equiv CSiPh_3$ in a similar molar ratio to $IrH_2(SiPh_3)(TFB)(PCy_3)$ is also observed. The formation of the alkenylsilyl complex $Ir\{C(SiPh_3)=CHPh\}(TFB)(PCy_3)$ is a result of the insertion of $PhC\equiv CSiPh_3$ into the Ir–H bond of the intermediate $IrH(TFB)(PCy_3)$. Complexes of this type are very rare. Eish et al. [42] have reported that at $-20°C$, chloroform solutions of titanocene dichloride yield $[Cp_2Ti\{C(SiMe_3)=CHPh\}]AlCl_4$, by treatment with $PhC\equiv CSiMe_3$ in the presence of CH_3AlCl_2. Tanaka and coworkers [43] have observed that alkynes undergo insertion reactions into the Me_3Si–Pt bond of $PtBr(SiMe_3)(PEt_3)_2$, to afford the β-alkenylsilyl derivatives $PtBr\{CR=CR(SiMe_3)\}(PEt_3)_2$. They have also observed [44] that the treatment of the bis (μ-silylene) complex $[Cp^*Ru(\mu\text{-}SiPh_2)(\mu\text{-}H)]_2$ with acetylene leads to the μ-2,5-1-disilaruthenacyclopentene complex $Cp^*Ru\{\mu\text{-}Si(Ph)_2CH=CHSiPh_2\}(\mu\text{-}H)_2RuCp^*$ as a result of the insertion of C_2H_2 into an Ru–Si bond of $[Cp^*Ru(\mu\text{-}SiPh_2)(\mu\text{-}H)]_2$. Jones et al. [45] have described the synthesis of $Cp^*Ru\{C(SiHMe_2)=CPh_2\}(PR_3)$, which can be viewed as a 1-silaallene stabilised by both metal ligation and interaction with a metal–hydrogen bond.

The addition of 1 equiv. of H_2SiPh_2 to $Ir(C_2Ph)(TFB)(PCy_3)$ leads to the dihydrido–silyl $IrH_2\{Si(C\equiv CPh)Ph_2\}(TFB)(PCy_3)$ (Scheme 11). The reaction is similar to the formation of the acetoxysilyl derivative $IrH_2\{Ph_2SiC(O)CH_3\}(TFB)(PCy_3)$ (Scheme 9). However, in this case, the participation of a silylene species as a reaction intermediate (path *b* of Scheme 10) is not very likely. It is well-known that electronic structures and reactivities of organic fragments change when they coordinate to transition metals to form organometallic complexes. For example, the coordination of $[RC\equiv C]^-$ to a metal centre, transfers the nucleophilicity from the α-carbon atom to the β-carbon atom [46]. Therefore the attack of the C_α carbon atom of the alkynyl group at the silicon atom of a silylene derivative does not seem likely, given the electrophilicity of both centres. Hence, it can be proposed that the formation of $IrH_2\{Si(C\equiv CPh)Ph_2\}(TFB)(PCy_3)$ occurs by initial oxidative addition of H_2SiPh_2 to $Ir(C_2Ph)(TFB)(PCy_3)$ to give $IrH(C_2Ph)(SiHPh_2)(TFB)(PCy_3)$, followed by the reductive elimination of $HSi(C\equiv CPh)Ph_2$ and subsequent oxidative addition of the Si–H bond of the new alkyne to $IrH(TFB)(PCy_3)$ (Scheme 11). A similar mechanism has been proposed for silane exchange reactions [47].

2.3.3. Hydrido–stannyl complexes

Complexes $Ir(XR')(TFB)(PCy_3)$ ($XR' = OMe$, OEt, O^iPr, OPh, S^nPr) react with $HSnPh_3$ and HSn^nBu_3 in a 1:2 molar ratio, to give the dihydrido (stannyl)–iridium(III) derivatives $IrH_2(SnR_3)(TFB)(PCy_3)$ (SnR_3=$SnPh_3$, Sn^nBu_3) which are related to the previously mentioned dihydrido(silyl)iridium(III) complexes $IrH_2(SiR_3)(TFB)(PR_3)$ [29].

These reactions most probably involve the oxidative addition of the stannanes to the starting materials to give $IrH(XR')(SnR_3)(TFB)(PCy_3)$ intermediates. Thus, the



Scheme 12.

subsequent elimination of $R'XSnR_3$ followed by the oxidative addition of a second stannane molecule to $IrH(TFB)(PCy_3)$ should afford $IrH_2(SnR_3)(TFB)(PCy_3)$ (Scheme 12).

The complex $IrH_2(SnPh_3)(TFB)(PCy_3)$ has been characterised by an X-ray crystallographic study. The most noticeable structural parameter is the Sn–Ir–P angle (129.46(3)°), which deviates significantly from the ideal value of 180°. This may be due to the different steric requirements, relatively small for the hydrides and comparatively large for the diene molecule and PCy_3 and $SnPh_3$ ligands. Angular distortions in hydrido complexes are not unusual. Thus, in the complex $IrH_2(SiEt_3)(COD)(AsPh_3)$, the angle between the triethylsilyl and the triphenylarsine ligands is 133.40(4)° [35b], and in the base-stabilised silylene derivative $IrH_2\{Si(OTf)Ph_2\}(TFB)(P^iPr_3)$ the angle between the $Si(OTf)Ph_2$ group and the triisopropyl–phosphine ligand is 129.51(7)° [20]. A similar observation has been reported for the complex $IrH_2(SnCl_3)(PPh_3)_3$, in which the major deviation from the ideal octahedral geometry arises from the P–Ir–P angle (145.95(9)°), involving two chemically equivalent phosphine groups, which are *pseudo–trans* to one other [48]. Values of about 150° have been also reported for the related angle in the complexes *mer*-$IrH_3(PPh_3)_3$ [49], $[(PPh_3)Au(\mu\text{-}H)IrH_2(PPh_3)_3]^+$ [50], *mer*-$[IrH_2(CO)(PPh_3)_3]^+$ [51] and $[IrH_2(PPh_3)_2(C_4H_8S)_2]^+$ [52]. The Ir–Sn distance (2.6122(5) Å) is also noteworthy. It is significantly lower than the value of 2.75 Å suggested for an iridium–tin single bond and thus indicates the presence of some partial multiple bond character [53].

In solution, the complexes $IrH_2(SnR_3)(TFB)(PCy_3)$ have a rigid structure only at low temperature. At r.t., they show behaviour similar to that previously mentioned for the related dihydrido(silyl) derivatives $IrH_2(SiR'_3)(TFB)(PR_3)$ (Eq. 7). However, the addition of P^iPr_3 to benzene-d_6 solutions of $IrH_2(SnR_3)(TFB)(PCy_3)$ (SnR_3 =

$SnPh_3$, Sn^nBu_3) does not affect the spectra of these compounds, suggesting that in this case the fluxional process does not require the dissociation of the phosphine ligand. The activation parameters for $IrH_2(SnPh_3)(TFB)(PCy_3)$, $IrH_2(Sn^nBu_3)(TFB)(PCy_3)$ and $IrH_2(SiPh_3)(TFB)(PCy_3)$ are given in Table 1.

For the silyl complex $IrH_2(SiPh_3)(TFB)(PCy_3)$, the large positive value of the entropy of activation (13.6 ± 2.6 eu) is in agreement with the dissociation of the phosphine ligand during the fluxional process, as has been previously mentioned, while for the stannyl derivatives the values of the entropy of activation, close to zero, are in agreement with the fact that the dissociation of the phosphine does not take place. If the dissociation of the phosphine from $IrH_2(SnR_3)(TFB)(PCy_3)$ does not occur during the intramolecular exchange of the diolefin atoms, it could be proposed that, for the stannyl compounds, the fluxional process involves the dissociation of one arm of the chelating tetrafluorobenzobarrelene diolefin, followed by rotation of the diene around the remaining iridium–olefin bond. This implies that the iridium–tetrafluorobenzobarrelene bond is more labile in $IrH_2(SnR_3)(TFB)(PCy_3)$ than in $IrH_2(SiPh_3)(TFB)(PCy_3)$. In support of this proposal, it has been found that the reaction of $IrH_2(SnPh_3)(TFB)(PCy_3)$ with carbon monoxide produces the displacement of the diene and the formation of $Ir(SnPh_3)(CO)_3(PCy_3)$ [29], while under the same conditions, the complex $IrH_2(SiPh_3)(TFB)(PCy_3)$ affords $Ir(\eta^1{:}\eta^2\text{-}C_{12}F_4H_7)(CO)_2(PCy_3)$ (Scheme 9). The complex $Ir(SiPh_3)(CO)_3(PCy_3)$, which is a rare example of a silyl–iridium(I) derivative [54], is prepared by reaction of $Ir\{\kappa^1\text{-}OC(O)CH_3\}(CO)_2(PCy_3)$ with $HSiPh_3$ [34].

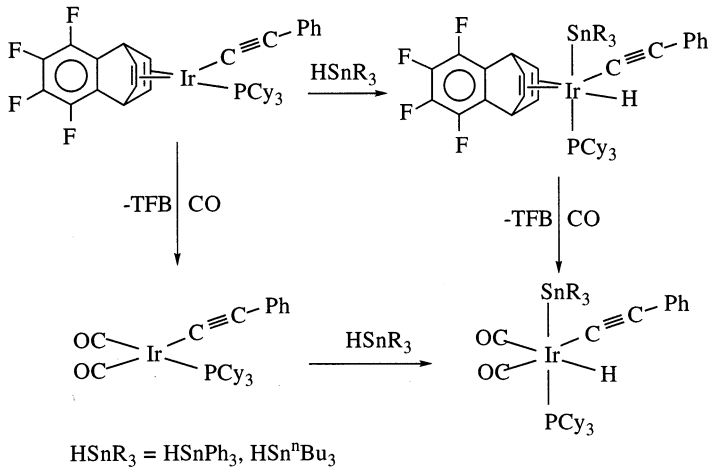
For late transition metal–silicon and metal–tin bonds some multiple bond character has previously been suggested [53,55]. This multiple bond character has been generally attributed to d^1–d^1 bonding involving donation of α-electron density from the transition metal to empty silicon or tin orbitals of appropriate symmetry. Because the energy difference between the iridium and tin d-orbitals (5d–5d) is smaller than that between the iridium and silicon d-orbitals (5d–3d), there should be a better iridium–tin overlap and, therefore, a stronger iridium–tin bond would be expected. The behaviour of $IrH_2(SnPh_3)(TFB)(PCy_3)$ and $IrH_2(SiPh_3)(TFB)(PCy_3)$ towards carbon monoxide is in agreement with this. The higher contribution of a d^1–d^1 interaction to the iridium–tin bond compared with the iridium–silicon bond could also explain the different behaviour of these

Table 1
Activation parameters for the fluxional process in complexes $IrH_2(ER_3)(TFB)(PCy_3)$ [29]

ER_3	T_c (K)	$\Delta G^{\ddagger}$ (kcal mol^{-1})[a]	$\Delta H^{\ddagger}$ (kcal mol^{-1})[b]	$\Delta S^{\ddagger}$ (eu)[b]
$SnPh_3$	273 ± 1	12.8 ± 0.1	13.4 ± 0.9	3.0 ± 3.0
Sn^nBu_3	293 ± 1	13.6 ± 0.1	12.7 ± 0.9	-1.6 ± 2.0
$SiPh_3$	263 ± 1	13.0 ± 0.1	16.5 ± 0.9	13.6 ± 2.6

[a] Calculated from T_c and Δv_0 with the equations $kc = (\pi/\sqrt{2})\Delta v_0$ and $\Delta G^{\ddagger}/RTc > \ln(\sqrt{2}R/\pi Nh) + \ln(T_c/\Delta v_0)$. Errors shown are propagated from the estimated errors in T_c.

[b] Calculated from the slopes and intercepts of the Eyring plots. Error ranges listed correspond to one standard deviation.



Scheme 13.

compounds in solution. The transfer of electron density from the iridium to the stannyl groups should increase the electron-donor capacity of the phosphine thus hindering its dissociation, while the capacity of the iridium to back bond to the diolefin should decrease, favouring the dissociation of one arm of the tetrafluorobenzobarrelene ligand. The lability of one arm of the diene in $IrH_2(SnR_3)(TFB)(PCy_3)$ may also be a result of the steric demands of the tin atom compared to the silicon one.

The alkynyl complex $Ir(C_2Ph)(TFB)(PCy_3)$ also reacts with $HSnPh_3$ and HSn^nBu_3. However, in this case, the reaction products are the hydrido–alkynyl derivatives $IrH(C_2Ph)(SnR_3)(TFB)(PCy_3)$ ($SnR_3 = SnPh_3$ or Sn^nBu_3). Under carbon monoxide atmosphere, these compounds yield the corresponding dicarbonyl complexes, which can also be obtained by oxidative addition of $HSnPh_3$ and HSn^nBu_3 to the dicarbonyl $Ir(C_2Ph)(CO)_2(PCy_3)$ (Scheme 13).

The exclusive and quantitative formation of $IrH(C_2Ph)(SnR_3)(TFB)(PCy_3)$ and $IrH(C_2Ph)(SnR_3)(CO)_2(PCy_3)$, with the hydrido and stannyl ligands mutually *cis* disposed, is in agreement with a concerted *cis* addition of $HSnR_3$ to $Ir(C_2Ph)(TFB)(PCy_3)$ and $Ir(C_2Ph)(CO)_2(PCy_3)$, with specific substrate orientation. The addition of the stannanes to the square–planar diolefin complex seems to take place along the olefin–Ir–P axis, with the tin atom on the olefinic bond (Fig. 6); the

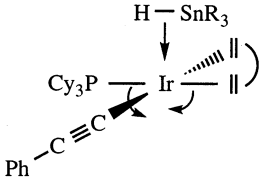


Fig. 6.

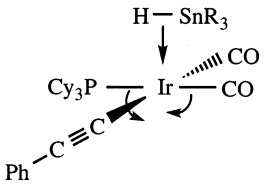


Fig. 7.

oxidative addition to the *cis*-dicarbonyl complex seems to occur along the OC–Ir–P axis, with the tin atom on the carbonyl group (Fig. 7). The basis of this preference is probably steric and involves minimising nonbonded interactions between the stannyl ligand and the cyclohexyl groups of the phosphine [29].

The reactions mentioned in this section, and those shown in Schemes 2–4, indicate that the products obtained (and their stereochemistry) from the oxidative addition of $HSnR_3$ to square–planar $IrXL_2(PR_3)$ (L_2 = TFB, 2CO) depend upon the nature of X, L_2 and $HSnR_3$, and are independent of the phosphine ligand.

2.3.4. Azavinylidene-bridged compounds

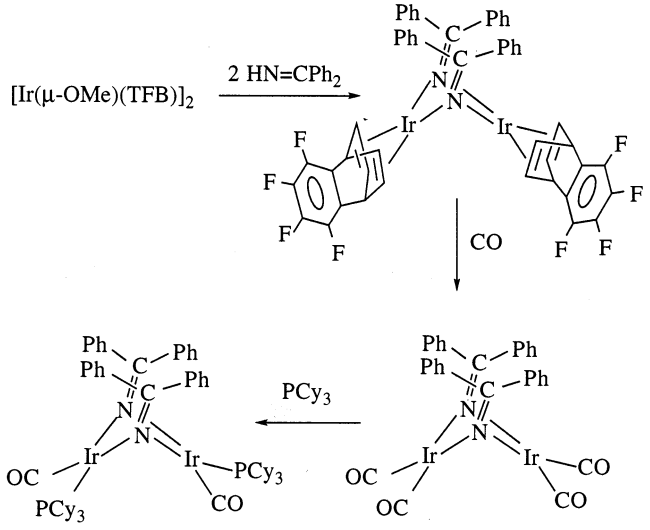
The azavinylidene-bridged compounds are usually synthesised by reaction of dinuclear complexes with diazirines. In this way, a variety of compounds of Ti [56], Mn [57], Fe [58] and Co [59] have been prepared. The methoxy-bridged dimer $[Ir(\mu\text{-OMe})(TFB)]_2$ is also a useful starting material to prepare azavinylidene-bridged iridium compounds. Thus, it reacts with a stoichiometric amount of benzophenone imine to give $[Ir(\mu\text{-N}=CPh_2)(TFB)]_2$ [27a]. The related 1,5-cyclooctadiene compound $[Ir(\mu\text{-N=}CPh_2)(COD)]_2$ is similarly prepared by reaction of $[Ir(\mu\text{-OMe})(COD)]_2$ with benzophenone imine.

The ^1H NMR spectrum of $[Ir(\mu\text{-N=}CPh_2)(TFB)]_2$ is temperature dependent. At r.t. it shows two signals due to the tetrafluorobenzobarrelene diolefin, whereas at -60°C, the spectrum contains four resonances, two aliphatic and two olefinic. This behaviour indicates a slow (on the NMR time scale) intramolecular exchange process which interconverts the equivalent (up/down) diolefin protons. This equilibration could be due to rotation of the terafluorobenzobarrelene ligand about the diene coordination axis, or to inversion of the folded structure at the position of the bridging ligands.

Bubbling carbon monoxide through dichloromethane solutions of $[Ir(\mu\text{-N=}CPh_2)(TFB)]_2$ results in the displacement of the coordinated diolefin and formation of the tetracarbonyl derivative $[Ir(\mu\text{-N=}CPh_2)(CO)_2]_2$, which reacts with tricyclohexylphosphine in a 1:2 molar ratio in hexane to give $[Ir(\mu\text{-N=}CPh_2)(CO)(PCy_3)]_2$ (Scheme 14).

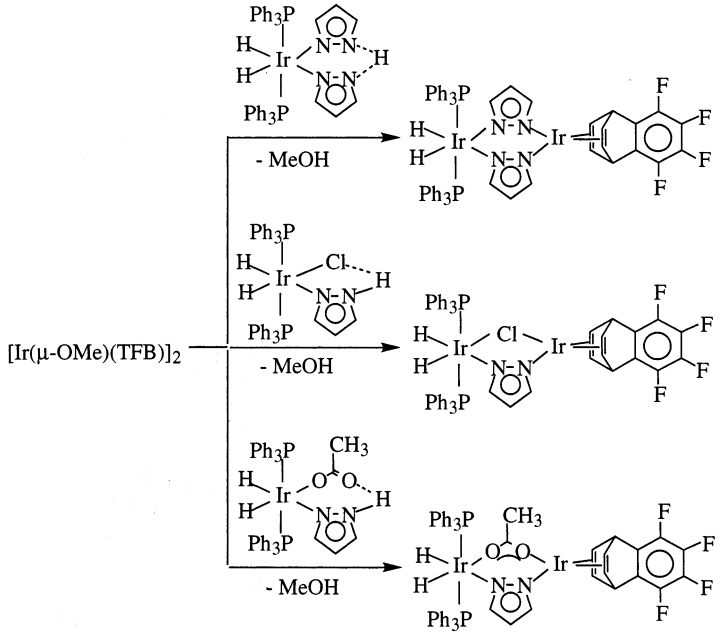
2.3.5. Dinuclear Ir(I)–Ir(III) compounds

Reaction of the iridium(III) complex $IrH_2(pz)(Hpz)(PPh_3)_2$ with the methoxy-bridged dimer $[Ir(\mu\text{-OMe})(TFB)]_2$ in refluxing tetrahydrofuran or acetone affords the neutral bimetallic-bis(pyrazolato)-bridged complex $(PPh_3)_2H_2Ir(\mu\text{-pz})_2Ir(TFB)$.



Scheme 14.

The related heterobridged dinuclear compounds $(PPh_3)_2H_2Ir(\mu\text{-}Cl)(\mu\text{-}pz)Ir(TFB)$ and $(PPh_3)_2H_2Ir(\mu\text{-}O_2CCH_3)(\mu\text{-}pz)Ir(TFB)$ (Scheme 15) have been similarly prepared, by reaction of the dimer $[Ir(\mu\text{-}OMe)(TFB)]_2$ with the mononuclear iridium-



Scheme 15.

(III) compounds $IrH_2Cl(Hpz)(PPh_3)_2$ and $IrH_2\{\kappa^1\text{-}OC(O)CH_3\}(Hpz)(PPh_3)_2$, respectively [60].

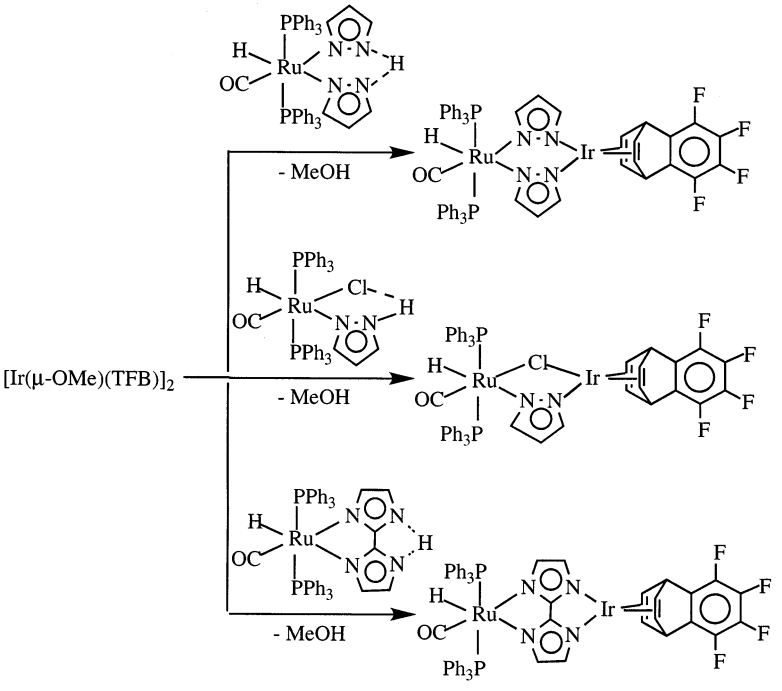
2.3.6. Dinuclear Ir(I)–Ru(II) compounds

Reaction of the ruthenium(II) complex $RuH(pz)(CO)(Hpz)(PPh_3)_2$ with $[Ir(\mu\text{-}OMe)(TFB)]_2$ affords the ruthenium(II)–iridium(I) derivative $(PPh_3)_2(CO)HRu(\mu\text{-}pz)_2Ir(TFB)$. The related compounds $(PPh_3)_2(CO)HRu(\mu\text{-}Cl)(\mu\text{-}pz)Ir(TFB)$ and $(PPh_3)_2(CO)HRu(\mu\text{-}bim)Ir(TFB)$ (Scheme 16) are similarly prepared by reaction of $[Ir(\mu\text{-}OMe)(TFB)]_2$ with $RuH(Cl)(CO)(Hpz)(PPh_3)_2$ [22] and $RuH(Hbim)(CO)(PPh_3)_2$ [61], respectively.

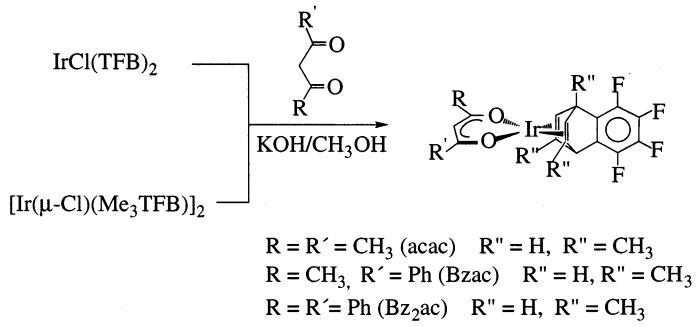
The structure of $(PPh_3)_2(CO)HRu(\mu\text{-}Cl)(\mu\text{-}pz)Ir(TFB)$ has been established by an X-ray diffraction study. The intermetalllic separation of 3.8907(6) Å excludes any direct intermetallic interaction. The planarity observed for the Ru–Cl–Ir–N–N ring, which additionally is roughly coplanar with the iridium square–planar coordination plane and with the equatorial plane of the octahedral environment of the ruthenium atom [22], is also remarkable.

2.4. β-Diketonato complexes

The complexes $IrCl(TFB)(TFB)_2$ and $[Ir(\mu\text{-}Cl)(Me_3TFB)]_2$ react with acetylace-



Scheme 16.

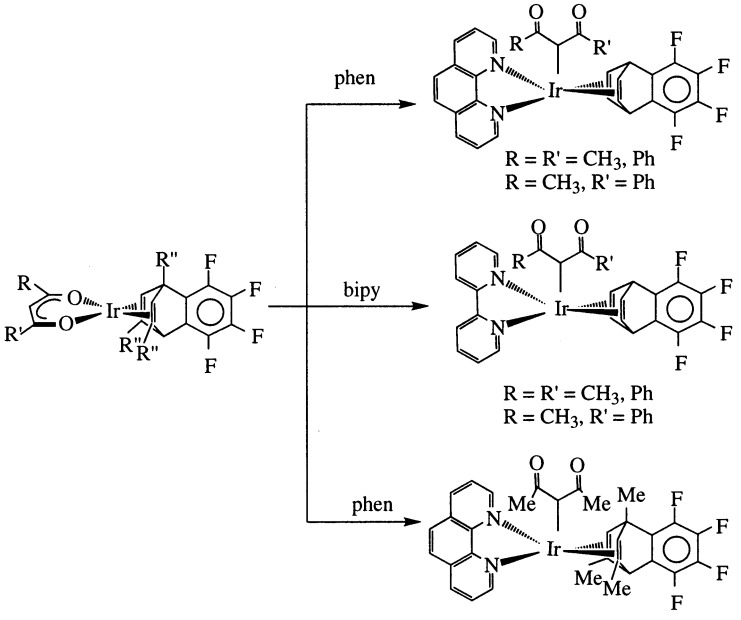


Scheme 17.

tone (Hacac), 1-phenyl-propane-1,3-dione (HBzac) or 1,3-diphenyl-propane-1,3-dione (HBz_2ac), in basic medium, to give square–planar complexes of formula Ir(β-diketonato)(diolefin) (Scheme 17) [18,62].

Treatment of Ir(β-diketonato)(diolefin) with 1,10-phenanthroline or 2,2′-bipyridine leads to five-coordinate iridium carbon-bonded diketonato complexes of the type Ir(β-diketonato-C^3)(diolefin)L_2 (diolefin = TFB, Me_3TFB) according to Scheme 18 [62].

The related 1,5-cyclooctadiene derivative Ir(acac-C^3)(COD)(phen) has been similarly prepared by reaction of Ir(acac)(COD) with 1,10-phenanthroline, and charac-



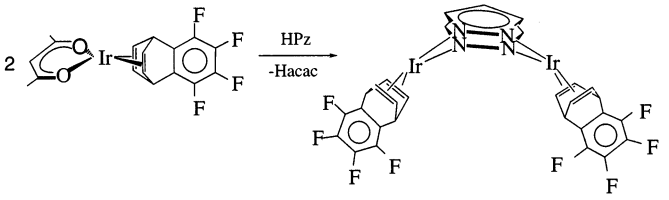
Scheme 18.

terised by standard X-ray methods. The iridium atom has a distorted pyramidal stereochemistry, with the nitrogen atoms of the phenanthroline and the midpoint of the olefin bonds of the cyclooctadiene in the base, while the apex is occupied by a σ-bonded carbon atom of the acetylacetonato group at a rather long distance (Ir–C = 2.420(6) Å) [63].

The formation and relative stability of the Ir(β-diketonato-C^3)(diolefin)L_2 complexes are dependent on all the involved ligands: thus, (i) for given diolefin and bidentate nitrogen donor ligands, the acac group seems to give stronger Ir–C^3 bonds than the Bz_2ac ligand; e.g. complex Ir(acac-C^3)(TFB)(bipy) is stable in dicloromethane solution, while complex Ir(Bz_2ac)(TFB)(bipy) reverts to the O-bonded complex Ir(Bz_2ac)(TFB); (ii) the phenanthroline ligand stabilises the Ir–C^3-bonded diketonate complexes more effectively than the bipyridine ligand, thus, complex Ir(Bz_2ac-C^3)(TFB)(phen) is prepared at r.t. by treating complex Ir(Bz_2ac)(TFB) with a stoichiometric amount of phenanthroline, while the synthesis of the related compound Ir(Bz_2ac–C^3)(TFB)(bipy) requires the use of low temperature (−15°C) and an excess of the nitrogen donor ligand; and (iii) the tetrafluorobenzobarrelene diolefin is a better ligand than the trimethyltetrafluorobenzobarrelene and 1,5-cyclooctadiene diolefins to stabilise these type of compounds. Thus, five-coordinate iridium complexes containing bipy and Me_3TFB or COD have not been isolated. This is in agreement with the previously mentioned greater ability of the Ir–TFB unit to stabilise five-coordinate iridium(I) complexes.

Some studies on the reactivity of the complex Ir(acac–C^3)(TFB)(phen) have been carried out [62]. The Ir–acac–C^3 bond of this complex can be broken by reactions with a variety of mineral acids and chloro complexes. The complex Ir(acac–C^3)(TFB)(phen) reacts with HCl or HBF_4 to give IrCl(TFB)(phen) or [Ir(TFB)(phen)]BF_4, respectively, and with [Rh(μ-Cl)(TFB)]$_2$ or IrCl(TFB)$_2$, to yield IrCl(TFB)(phen) or M(acac)(TFB) (M = Rh, Ir). The Ir–acac–C^3 bond of the complex Ir(acac–C^3)(TFB)(phen) can also be broken by reaction with iodine. In this case, the reaction product is the cation [IrI_2(COD)(phen)]$^+$ with the iodine atoms mutually *trans* disposed, as has been shown by an X-ray diffraction study.

In addition, it should be mentioned that the square–planar β-diketonato complex Ir(acac)(TFB) reacts with a stoichiometric amount of pyrazole to afford the dimer [Ir(μ-pz)(TFB)]$_2$ (Eq. 8) [22]:



(8)

2.5. Cationic complexes

In the previous sections, we have shown that the Ir–TFB unit has a greater ability than the Ir–COD unit to stabilise five-coordinate complexes. No type of compounds illustrates this better than the cationic species, as reflected in the formation of the derivatives $[Ir(TFB_2)L]^+$ and $[Ir(TFB)L_2(PR_3)]^+$, which have no analogues in the 1,5-cyclooctadiene chemistry, and in the necessity for using particular synthetic strategies to prepare the traditionally $[Ir(diolefin)L_2]^+$, $[Ir(diolefin)L(PR_3)]^+$ and $[Ir(diolefin)(\eta^6\text{-arene})]^+$ stoichiometries, when the diolefin is tetrafluorobenzobarrelene.

2.5.1. *$[Ir(TFB)_2L]ClO_4$ and $[Ir(COD)(TFB)L]ClO_4$ complexes*

The complex $IrCl(TFB)_2$ reacts with $AgClO_4$ to give $Ir(OClO_3)(TFB)_2$ (Eq. (9)) [19]. In the solid state, this complex contains a bonded perchlorato ligand, as revealed by the IR spectrum in Nujol, which is characteristic for a covalent bonded group with C_{3v} symmetry [64]. In contrast, the complexes $[Ir(COD)_2]ClO_4$ [26] and $[Ir(Me_3TFB)_2]ClO_4$ [19] are square planar species:

$$IrCl(TFB)_2 + AgClO_4 \rightarrow Ir(OClO_3)(TFB)_2 + AgCl \quad (9)$$

In acetone solution the perchlorato ligand is displaced and the measured conductivities are as expected for a 1:1 electrolyte. The same behaviour has also been observed for $Ir(OClO_3)(COD)(TFB)$, which has been prepared by reaction of $[Ir(\mu\text{-}Cl)(COD)]_2$ with silver perchlorato in the presence of tetrafluorobenzobarrelene (Eq. (10)) [65]:

$$[Ir(\mu\text{-}Cl)(COD)]_2 + 2AgClO_4 + 2TFB \rightarrow 2Ir(OClO_3)(COD)(TFB) + 2AgCl \quad (10)$$

The addition of an excess or a stoichiometric amount of ligands such as triphenylarsine, triphenylstibine, acetonitrile, dimethylsulfoxide, diethylsulfide and triphenylphosphinesulfide, to dichloromethane suspensions of $Ir(OClO_3)(TFB)_2$, leads to the displacement of the perchlorato group from its coordination site, and the formation of five coordinate complexes of type $[Ir(TFB)_2L]ClO_4$ (Eq. (11)) [19]:

$$Ir(OClO_3)(TFB)_2 + L \rightarrow [Ir(TFB)_2L]ClO_4 \quad (11)$$

$L = AsPh_3$, $SbPh_3$, NCMe, Me_2SO, SEt_2, $SPPh_3$.

The perchlorato group of the complex $Ir(OClO_3)(COD)(TFB)$ can be also displaced by nitrile ligands to afford $[Ir(COD)(TFB)(NCR)]ClO_4$, which can also be prepared by reaction of the corresponding square–planar compounds $[Ir(COD)(NCR)_2]ClO_4$ with tetrafluorobenzobarrelene (Eq. (12)) [65]:

$$[Ir(COD)(NCR)_2]^+ + TFB \rightarrow [Ir(COD)(TFB)(NCR)]^+ + NCR \quad (12)$$

$NCR = NCPh$, $NCCH_2Ph$, NCMe.

2.5.2. $[Ir(TFB)L_2]^+$ complexes

A direct and convenient method, which is also general, for preparing cationic complexes of the type $[Ir(COD)L_2]^+$, is to treat the dimeric compound $[Ir(\mu\text{-}Cl)(COD)]_2$ with an equimolar amount of a silver salt in the presence of the corresponding ligands L [66]. The application of a similar method to obtain $[Ir(TFB)L_2]^+$ compounds is not possible due to the stoichiometry of the primary material, $IrCl(TFB)_2$, in the tetrafluorobenzobarrelene chemistry, and also due to the fact that only some types of ligands have the ability to remove a tetrafluororobenzobarrelene diolefin from the coordination sphere of the iridium. Thus, three synthetic strategies have been used to prepare $[Ir(TFB)L_2]^+$ complexes. These strategies depend upon the nature of the donor atom of the ligands L [19].

2.5.2.1. P-donor and N-donor (pyridine type) ligands. Addition of an excess of 2-methylpyridine or quinoline, or the stoichiometric amounts of triphenylphosphine or 1,10-phenanthroline to dichloromethane suspensions of $Ir(OClO_3)(TFB)_2$ leads to the displacement of one molecule of tetrafluorobenzobarrelene and to the formation of the square–planar complexes $[Ir(TFB)L_2]ClO_4$ (Eq. (13)):

$$Ir(OClO_3)(TFB)_2 + 2L \text{ (or } L_2) \rightarrow [Ir(TFB)L_2]ClO_4 + TFB \quad (13)$$

$L = 2\text{-Mepy, quin, } PPh_3;\ L_2 = \text{phen.}$

Carbon monoxide also has the ability to remove a tetrafluorobenzobarrelene molecule from $Ir(OClO_3)(TFB)_2$. Thus, bubbling this gas through a dichloromethane suspension of $Ir(OClO_3)(TFB)_2$ leads to a white stable substrate of formula $[Ir(TFB)(CO)_3]ClO_4$ (Eq. (14)):

$$Ir(OClO_3)(TFB)_2 + 3CO \rightarrow [Ir(TFB)(CO)_3]ClO_4 + TFB \quad (14)$$

2.5.2.2. Monodentate As- and Sb-donor ligands. Triphenylarsine and triphenylstibine are not capable of removing a diolefin ligand from $Ir(OClO_3)(TFB)_2$. However, they are capable of displacing a tetrafluorobenzobarrelene ligand from $IrCl(TFB)_2$ to afford $IrCl(TFB)(EPh_3)_2$ (Scheme 5). As a result of this, the complexes $[Ir(TFB)(EPh_3)_2]ClO_4$ (E = As, Sb) have been obtained by reaction of $IrCl(TFB)(EPh_3)_2$ with $AgClO_4$ (Eq. (15)):

$$IrCl(TFB)(EPh_3)_2 + AgClO_4 \rightarrow [Ir(TFB)(EPh_3)_2]ClO_4 + AgCl \quad (15)$$

In the presence of tetrafluorobenzobarrelene, the complexes $[Ir(TFB)(EPh_3)_2]ClO_4$ evolve into the five-coordinate derivatives $[Ir(TFB)_2(EPh_3)]ClO_4$. So, the formation 'in situ' of $IrCl(TFB)(EPh_3)_2$, by addition of $AsPh_3$ or $SbPh_3$ to $IrCl(TFB)_2$, and the subsequent treatment of the mixture with an equimolar amount of a silver salt, is not an efficient method to prepare $[Ir(TFB)(EPh_3)_2]^+$. However, this synthetic strategy has been useful to obtain $[Ir(TFB)(Hpz)_2]BF_4$ [67] and $[Ir(TFB)\{\kappa^2\text{-}^i Pr_2PCH_2CH_2L\}]BF_4$ (L = OMe, NMe_2) [68].

2.5.2.3. S-donor and N-donor (nitrile type) ligands. The square planar complexes $[Ir(TFB)L_2]BF_4$ containing these relatively weak ligands, incapable of displacing a tetrafluorobenzobarrelene molecule from $IrCl(TFB)_2$ or $Ir(OClO_3)(TFB)_2$, can be obtained by treating Ir(acac)(TFB) with $HBF_4{\cdot}OEt_2$ in the presence of the corresponding ligand, according to Eq. (16):

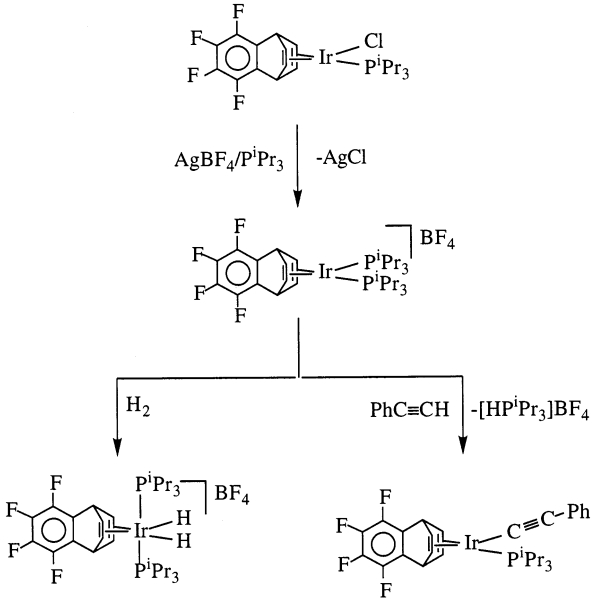
$$Ir(acac)(TFB) + 2L \text{ (or } L_2) + HBF_4 \rightarrow [Ir(TFB)L_2]BF_4 + Hacac \quad (16)$$

$L = SEt_2$, 4-MeObzn; L_2 = sucn (succinonitrile).

2.5.3. $[Ir(TFB)(P^iPr_3)_2]BF_4$

We have previously mentioned that the dimeric complex $[Ir(\mu\text{-}Cl)(COD)]_2$ is a key starting material for the preparation of $[Ir(COD)(PR_3)_n]^+$. The value of *n* in these systems depends upon the cone angle of the phosphine ligand. Thus, the five-coordinate complexes $[Ir(COD)(PR_3)_3]^+$ are stabilised by phosphine ligands with cone angles smaller than 130°, while the four coordinate derivatives $[Ir(COD)(PR_3)_2]^+$ are obtained when the cone angle of the phosphorus donor ligand is between 130 and 145°. Very bulky phosphine ligands, e.g. P^iPr_3, do not form cations of this type [69].

In contrast to the Ir–COD unit, the Ir–TFB moiety allows the formation of four-coordinate cation $[Ir(TFB)(P^iPr_3)_2]^+$, which has been further characterised by an X-ray diffraction analysis [70]. The complex $[Ir(TFB)(P^iPr_3)_2]BF_4$ is prepared in high yield (93%) by reaction of $IrCl(TFB)(P^iPr_3)$ with $AgBF_4$ in the presence of triisopropylphosphine (Scheme 19).



Scheme 19.

Two features of the structure of the complex $[Ir(TFB)(P^iPr_3)_2]BF_4$ complex must be pointed out: (i) the relatively large value of the P–Ir–P angle (102.7(1)°), which can be explained by the fact that the two phosphine ligands, *cis* disposed, experience a large steric hindrance as a result of the large cone angle of the triisopropylphosphine group (160°) [71], and (ii) the tetrafluorobenzobarrelene bite angle of 67.9(5)°, which is significantly smaller than the 1,5-cyclooctadiene bite angle in Ir(η^4-COD) complexes (86(3)°) [72]. Thus, the larger space required by the 1,5 cyclooctadiene diolefin in comparison with tetrafluorobenzobarrelene could explain why, with 1,5-cyclooctadiene it has not been possible to stabilise a related compound to $[Ir(TFB)(P^iPr_3)_2]^+$.

In dichloromethane as solvent, the complex $[Ir(TFB)(P^iPr_3)_2]BF_4$ and the related cations $[Ir(COD)(PR_3)_2]^+$ show different behaviour toward molecular hydrogen. While the complex $[Ir(TFB)(P^iPr_3)_2]BF_4$ reacts with molecular hydrogen to give the dihydrido derivative *cis*, *trans*-$[IrH_2(TFB)(P^iPr_3)_2]BF_4$ (Scheme 19), the reaction of the cations $[Ir(COD)(PR_3)]^+$ with hydrogen affords *cis*–*cis*-$[IrH_2(COD)(PR_3)_2]^+$. The complexes *cis*, *trans*-$[IrH_2(COD)(PR_3)_2]^+$ can be prepared by reaction of $[Ir(COD)(PR_3)_2]^+$ with molecular hydrogen in the presence of 1,5-cyclooctadiene, or alternatively by treatment of the solvated compounds $[IrH_2(acetone)_2(PR_3)_2]^+$ with 1,5-cyclooctadiene [73]. The complexes $[Ir(DCT)(PR_3)_2]^+$ show a similar behaviour to that of $[Ir(COD)(PR_3)_2]^+$ [14].

The complex $[Ir(TFB)(P^iPr_3)_2]^+$ also reacts with phenylacetylene. In this case, the obtained product is the square–planar alkynyl derivative $Ir(C_2Ph)(TFB)(P^iPr_3)$ (Scheme 19), related to the tricyclohexylphosphine compounds shown in Scheme 7.

2.5.4. [Ir(TFB)L(PR$_3$)]$^+$ complexes

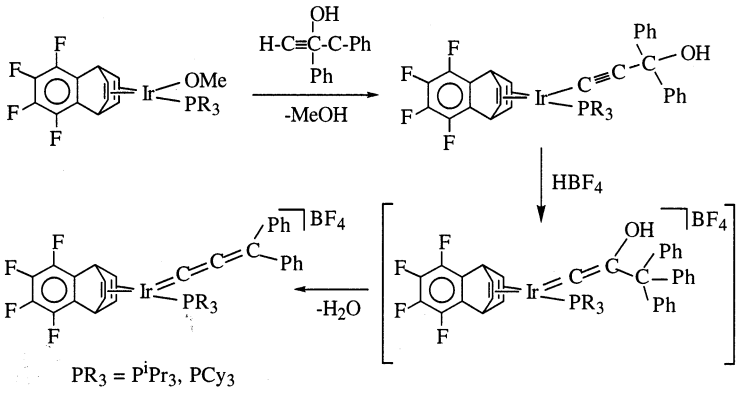
The addition of a stoichiometric amount of triphenylphosphine to square–planar complexes of the type $[Ir(TFB)L_2]^+$, containing monodentated N-, As- or Sb-donor ligands, produces the displacement of one molecule of the corresponding monodentate ligand, and the formation of the square–planar derivatives $[Ir(TFB)L(PPh_3)]^+$ (Eq. (17)) [9].

$$[Ir(TFB)L_2]^+ + PPh_3 \rightarrow [Ir(TFB)L(PPh_3)]^+ + L \quad (17)$$

L = 2-Mepy, quin, 4-MeObzn, $AsPh_3$, $SbPh_3$.

Recently, the diphenylallenylidene complexes $[Ir(TFB)(C{=}C{=}CPh_2)(PR_3)]BF_4$ ($PR_3 = P^iPr_3$ or PCy_3) have also been synthesised [27b]. These compounds, which are the only examples of mixed-ligand complexes of the type $[Ir(diene)L(PR_3)]^+$ containing an unsaturated η^1-carbon ligand, and the first examples reported of iridium–allenylidene derivatives, are prepared according to Scheme 20.

Although the alkynol 1,1-diphenyl-2-propyn-1-ol contains two relatively acidic protons, the H–C(sp) and H–OC hydrogen atoms, it selectively reacts with the methoxide group of the complexes $Ir(OMe)(TFB)(PR_3)$ to give $Ir\{C{\equiv}CC(OH)Ph_2\}(TFB)(PR_3)$, which afford $[Ir(TFB)(C{=}C{=}CPh_2)(PR_3)]BF_4$ ($PR_3 = P^iPr_3$, PCy_3) upon protonation with $HBF_4{\cdot}OEt_2$. From a mechanistic point of view, these allenylidene compounds could be a consequence of the direct protonation of the –OH group of the alkynyl ligand, or most probably the result



Scheme 20.

of the spontaneous dehydration of hydroxyvinylidene intermediates, which should be generated by electrophilic attack of the proton of the acid at the β-carbon atom of the alkynyl ligand of the starting complexes. In this context, it should be mentioned that (i) the addition of electrophiles to metal alkynyl compounds is a general method of preparing vinylidene compounds and (ii) the dehydration of hydroxyvinylidene complexes to yield allenylidene derivatives is a well-known process [74].

Five-coordinate mixed-ligand complexes of the type $[Ir(TFB)(phen)L]^+$ have also been reported. They are prepared by reaction of the square–planar cation $[Ir(TFB)(phen)]^+$ with the corresponding ligand L (Eq. (18)) [19]:

$$[Ir(TFB)(phen)]^+ + L \rightarrow [Ir(TFB)(phen)L]^+ \quad (18)$$

$L = PPh_3$, $AsPh_3$, $SbPh_3$, $P(OPh)_3$.

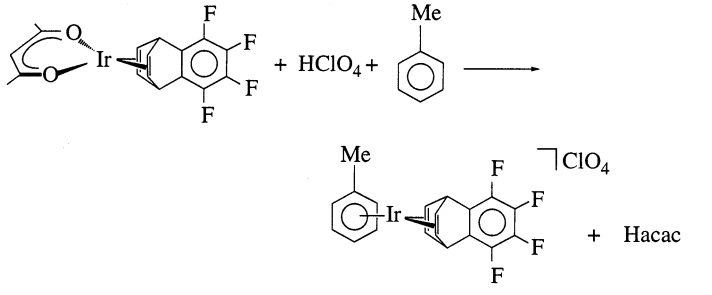
2.5.5. [Ir(TFB)(η⁶-arene)]⁺ complexes

The complex $IrCl(TFB)_2$ is an useful starting material for preparing dimethyl-, trimethyl-, tetramethyl- and hexamethyl–arene iridium(I) complexes. Thus, the treatment under reflux of an acetone suspension of $IrCl(TFB)_2$ with $AgBF_4$ and the corresponding arene produces the displacement of one molecule of tetrafluorobenzobarrelene from the starting material, and the formation of $[Ir(TFB)(\eta^6\text{-arene})]BF_4$ (Eq. (19)) [16].

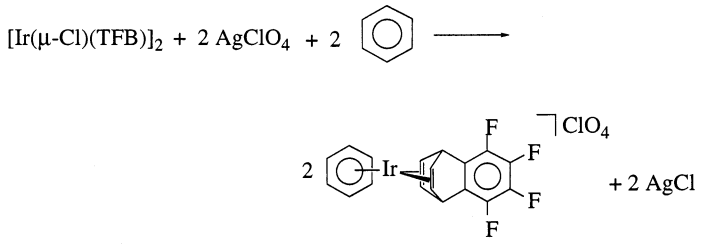
$$IrCl(TFB)_2 + AgBF_4 + arene \rightarrow [Ir(TFB)(\eta^6\text{-arene})]BF_4 + TFB + AgCl \quad (19)$$

arene = Me_6C_6, 1,2,4,5-$Me_4C_6H_2$, 1,2,3-$Me_3C_6H_3$, 1,2,4-$Me_3C_6H_3$, 1,4-$Me_2C_6H_4$, 1,3-$Me_2C_6H_4$, 1,2-$Me_2C_6H_4$.

Tetrafluorobenzobarrelene–iridium(I) arene complexes with lower electron density in the ring (MeC_6H_5 and C_6H_6) can be prepared by reaction of the acetylacetonato complex Ir(acac)(TFB) with $HClO_4$ in the presence of the arene (Eq. 20), or alternatively by treatment of the dimer $[Ir(\mu\text{-Cl})(TFB)]_2$ with an equimolar amount of a silver salt, also in the presence of the corresponding arene ligand (Eq. 21) [18]:



(20)

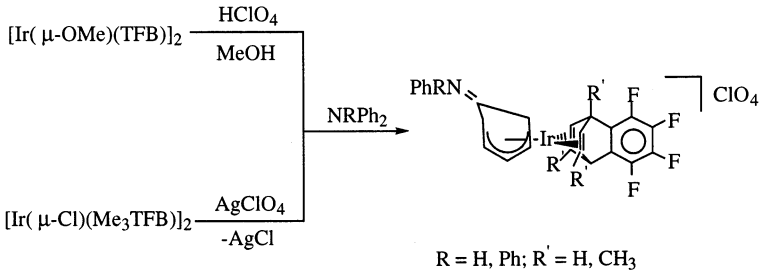


(21)

The latter method, using the trimethyltetrafluorbenzobarrelene complex [Ir(μ-Cl)(Me_3TFB)]$_2$ as starting material, leads to the synthesis of trimethyltetrafluorobenzobarrelene–iridium(I) arene complexes with a wide variety of arene ligands, including Me_6C_6, 1,2,4,5-$Me_4C_6H_2$, 1,3,5-$Me_3C_6H_3$, 1,2,4-$Me_3C_6H_3$, 1,4-$Me_2C_6H_4$, 1,3-$Me_2C_6H_4$, 1,2-$Me_2C_6H_4$, MeC_6H_5, C_6H_6, 1,4$(OH)_2C_6H_4$, acetophenone, tetraline, naphthalene, biphenyl, indene, and 1,10-dihydroanthracene.

The formation of the complexes [Ir(TFB)(η^5-C_6H_5NRPh)BF_4 and [Ir(Me_3TFB)-(η^5-C_6H_5NRPh)]BF_4 (R = H, Ph) has also been reported (Scheme 21).

The tetrafluorobenzobarrelene derivatives have been prepared by reaction of the dimer [Ir(μ-OMe)(TFB)]$_2$ with HBF_4·OEt_2 and amine, whereas the trimethyltetrafluorobenzobarrelene compounds have been synthesised by the procedure shown in Eq. 21, using the complex [Ir(μ-Cl)(Me_3TFB)]$_2$ as starting material [18]. The crystal structure of [Ir(TFB)(η^5-C_6H_5NRPh)]BF_4 and the spectroscopic data of the above mentioned [Ir(Me_xTFB)(η^5-C_6H_5NRPh)]BF_4 complexes clearly indicate a



Scheme 21.

distortion of the coordinated arene towards an unusual η^5-coordination iminocyclohexyl form [18].

2.6. Catalytic activity

Several mononuclear and dinuclear iridium–tetrafluorobenzobarrelene complexes show catalytic activity. The studied reactions include hydrogen transfer from 2-propanol to ketones, reduction of olefins and terminal alkynes with molecular hydrogen, addition of silanes to olefins and alkynes, and addition of stannanes to alkynes.

2.6.1. Hydrogen transfer from 2-propanol to ketones

In the presence of potassium hydroxide, the square planar cationic complexes $[Ir(TFB)L_2]^+$ catalyse the hydrogen transfer from 2-propanol to acetophenone. After 1 h of reaction the extent of reduction of ketone is 10–30% for monodentate N-donor ligands, and for other monodentate ligands it decreases in the sequence $PPh_3 > AsPh_3 > SbPh_3$. Bidentate ligands give more active systems, especially 1,10-phenanthroline and 2,2′-bipyridine [16].

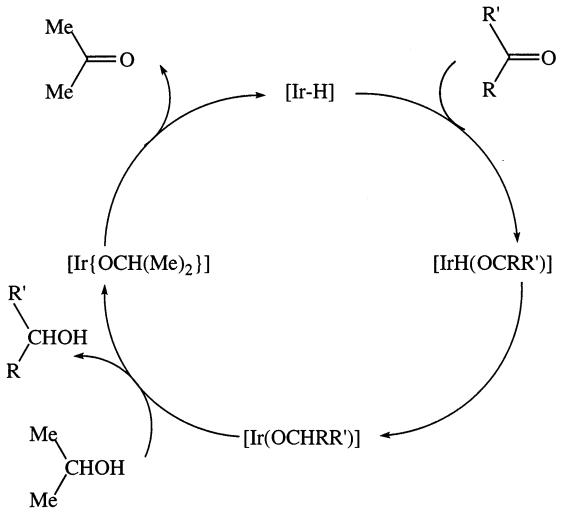
The presence of base in the catalytic solution is related to the formation of an $Ir–OCH(CH_3)_2$ intermediate which undergoes a β-elimination process to give IrH_xL_2 species [75,77c]. In agreement with this, it has been observed that the cation $[Ir(TFB)(PPh_3)_2]^+$ reacts with a potassium hydroxide 2-propanol solution to afford $IrH(TFB)(PPh_3)_2$ and acetone, which catalyses the reduction of ketones in absence of the base [28].

The species $IrH(TFB)L_2$ are coordinatively saturated, and therefore activation is needed to initiate the catalytic reaction. This activation involves the reduction of the coordinated diene, leading to the unsaturated complexes IrH_xL_2, which initiate the catalytic cycle. It has been proposed that the catalysis involves four steps (Scheme 22) [76]: (i) coordination of the ketone to the coordinatively unsaturated metal centre; (ii) formation of an alkoxy metal intermediate by hydrogen migration from the metal to the ketonic double bond; (iii) exchange of the alkoxy group by reactions with the alcohol, which acts as solvent; and (iv) a β-elimination process.

This cycle is general for platinum–metal catalysts of the type MH_xL_y [77].

The heterobinuclear complex $(PPh_3)_2(CO)HRu(\mu\text{-}Cl)(\mu\text{-}pz)Ir(TFB)$ catalyses the hydrogen transfer from 2-propanol to cyclohexanone. The reaction is first order in terms of catalyst concentration, suggesting that the nuclearity of the catalyst precursor remains unchanged during the catalysis. The addition of the non-active homodinuclear complex $[Ir(\mu\text{-}pz)(TFB)]_2$ to solutions of $(PPh_3)_2(CO)HRu(\mu\text{-}Cl)(\mu\text{-}pz)Ir(TFB)$ causes an increase of the initial reduction rate of cyclohexanone up to a maximum value of 0.5 mol cyclohexanol (mol Ru)$^{-1}$ min^{-1} [22].

The heterobinuclear complex $(PPh_3)(CO)HRu(\mu\text{-}Cl)(\mu\text{-}pz)Ir(COD)$, containing the Ir–COD unit, is also an active catalyst for the hydrogen transfer reaction from 2-propanol to cyclohexanone. However, under the catalytic conditions, the redistribution reaction shown in Eq. (22) occurs in this case. This is in agreement with observations indicating that the stability of the heterobridged $M(\mu\text{-}Cl)(\mu\text{-}pz)M$



Scheme 22.

framework is lower than that of the homobridged $M(\mu\text{-pz})_2M$ one [78] and that the heterobinuclear complexes containing the Ir–TFB unit bonded to the other metal atom through a chloride or pyrazolato bridge are more stable than those with the Ir–COD unit [22,79]:

$$(PPh_3)_2(CO)HRu(\mu\text{-Cl})(\mu\text{-pz})Ir(COD) \rightleftharpoons 2RuHCl(CO)(PPh_3)_2 + [Ir(\mu\text{-pz})(COD)]_2 \quad (22)$$

2.6.2. Hydrogenation of olefins and terminal alkynes

The complex $[Ir(TFB)(P^iPr_3)_2]BF_4$ has been found to be an active catalyst for the reduction of unsaturated organic substrates by molecular hydrogen, in dichloromethane as solvent [70]. The related cations $[Ir(COD)(PR_3)_2]^+$ are also active catalyst precursors [80]. However there is a significant difference in versatility between the tetrafluorobenzobarrelene and 1,5-cyclooctadiene systems. The cations $[Ir(COD)(PR_3)_2]^+$ are excellent catalysts for the reduction of olefins, but substrates such as styrene, stilbene, and α-methylstyrene, cannot be reduced due to the formation of arene derivatives [81]. In contrast to $[Ir(COD)(PR_3)_2]^+$, the complex $[Ir(TFB)(P^iPr_3)_2]BF_4$ is an active catalyst for the hydrogenation of styrene to ethylbenzene. The reduction rate of this olefin is even faster than that observed for the reduction of 1-hexene, cyclohexene or 2,3-dimethyl-2-butene. Although the reduction of 2,3-dimethyl-2-butene is slower than that of unhindered olefins, deactivation of $[Ir(TFB)(P^iPr_3)_2]BF_4$ is not observed. This is the other significant difference with regard to the $[Ir(COD)(PR_3)_2]^+$ cations, which in the presence of hindered olefins undergo an irreversible deactivation, as a result of the formation of the $[(PR_3)_2HIr(\mu\text{-H})_3IrH(PR_3)_2]^+$ dimers [80a,b]. So the complex $[Ir(TFB)(P^iPr_3)_2]BF_4$ is not only a more versatile catalyst than $[Ir(COD)(PR_3)_2]^+$ but also more stable.

In general, the hydrogenation of terminal alkynes catalysed by $[M(COD)(PR_3)_2]^+$ (M = Rh, Ir) systems is not easy [82]. In this sense, it has been proposed that the terminal alkynes, which are fairly acidic, destroy the active species by formation of metal–alkynyl derivatives [82a]. Despite the fact that the complex $[Ir(TFB)(P^iPr_3)_2]BF_4$ reacts with phenylacetylene to give $Ir(C_2Ph)(TFB)(P^iPr_3)$ (Scheme 19), it is a very active and highly selective catalyst for the reduction of phenylacetylene. In dichloromethane solution at 25°C and atmospheric pressure, selectivities close to 80% are achieved for the hydrogenation of the alkyne to the alkene.

Under the same conditions, selectivities close to 100% are achieved for the hydrogenation of phenylacetylene to styrene using the complex $[Ir(TFB)\{\kappa^2\text{-}^iPr_2PCH_2CH_2OMe\}]BF_4$ as catalyst. In contrast to $[Ir(TFB)\{\kappa^2\text{-}^iPr_2PCH_2CH_2OMe\}]BF_4$, the derivative $[Ir(TFB)\{\kappa^2\text{-}^iPr_2PCH_2CH_2NMe_2\}]BF_4$ is inactive [68].

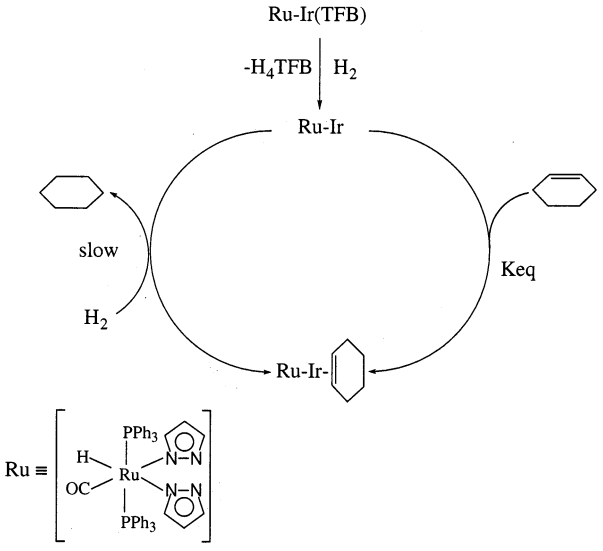
The complex $[Ir(TFB)\{\kappa^2\text{-}^iPr_2PCH_2CH_2OMe\}]BF_4$ is also a very effective catalyst for the hydrogenation of olefins. In dichloromethane as solvent, at 25°C, and under atmospheric pressure of hydrogen, the initial reduction rates of 0.2 M solutions of 1-hexene, cyclohexene, and 2,3-dimethyl-2-butene, with 1.0×10^{-3} M of catalyst, are greater than 6.8×10^{-4} M s^{-1}. The complex $[Ir(TFB)\{\kappa^2\text{-}^iPr_2PCH_2CH_2NMe_2\}]BF_4$ catalyses the hydrogenation of 1-hexene at the same rate as $[Ir(TFB)\{\kappa^2\text{-}^iPr_2PCH_2CH_2OMe\}]BF_4$, while the reduction of cyclohexene to cyclohexane is about one order of magnitude slower than the reduction of 1-hexene.

The hydrogenation of unsaturated organic substrates catalysed by dinuclear compounds containing the Ir–TFB unit has also been described. At 60°C, 2-propanol-toluene (1:1) solutions of the heterobinuclear complex $(PPh_3)_2(CO)HRu(\mu\text{-}pz)_2Ir(TFB)$ catalyse the hydrogenation of cyclohexene to cyclohexane [67]. The reaction shows an induction period which can be removed by treatment of the catalyst precursor solutions with molecular hydrogen for 1 h at 60°C. This induction period is related to the reduction of the diolefin coordinated to the iridium atom. Thus, under catalytic conditions, the species $(PPh_3)_2(CO)HRu(\mu\text{-}pz)_2IrS_x$, which has been characterised by ^1H NMR spectroscopy, is formed. In agreement with this, it has also been observed that the complex $(PPh_3)_2(CO)HRu(\mu\text{-}pz)_2Ir(TFB)$ catalyses the hydrogenation of tetrafluorobenzobarrelene. For the reduction of cyclohexene the experimental data fit a rate expression of the form:

$$\frac{-\,d[\text{cyclohexene}]}{dt} = k_{23}[\text{catalyst}]\,[\text{cyclohexene}]\,P(H_2) \qquad (23)$$

Eq. (23) is consistent with the mechanism shown in Scheme 23.

This mechanism is a standard unsaturated mechanism, and it was previously proposed, for example, for the hydrogenation of alkenes catalysed by the rhodium(I) mononuclear complex $[Rh(dppe)S_x]^+$ [83]. Interestingly, the complex $(PPh_3)_2(CO)HRu(\mu\text{-}pz)_2Ir(TFB)$ is a more active catalyst than the mononuclear parent compounds $RuH(pz)(CO)(Hpz)(PPh_3)_2$ and $[Ir(TFB)(Hpz)_2]BF_4$. Under the catalytic conditions previously mentioned, the activity of the mononuclear com-



Scheme 23.

pounds is rather poor; thus, after 24 h, the conversion of cyclohexene to cyclohexane is no more than 4%.

The significant modification of the catalytic activity of the mononuclear iridium fragment by bonding to the $RuH(CO)(PPh_3)_2$ unit has been rationalised on the basis of electronic communication between the metal centres through the bridging ligands [67]. The replacement of the acid protons of the pyrazole ligands in the mononuclear iridium complex, $[Ir(TFB)(Hpz)_2]^+$, by the ruthenium unit produces a decrease in the electron-donor capacity of the pyrazole towards the iridium atom and hence a flow of the electron density from the iridium atom to the ruthenium, as evidenced by the reduction of $\nu(CO)$ by 13 cm^{-1} in $(PPh_3)_2(CO)HRu(\mu\text{-}pz)_2Ir(TFB)$ compared with $RuH(pz)(CO)(Hpz)(PPh_3)_2$ [61]. This reduction of electron density on the iridium atom is responsible for its activation for catalysis, mainly in terms of the addition of hydrogen. Thus, it is known that the hydrogen addition process on mononuclear iridium–diolefin compounds is inhibited by relatively electron-donating ligands, but occurs with relatively electron accepting ligands [84].

2-Propanol–toluene (3:1) solutions of the dimer $[Ir(\mu\text{-}pz)(TFB)]_2$ also catalyse the hydrogenation of cyclohexene to cyclohexane at 60°C [67]. In this case, the reaction again shows an induction period that disappears when the catalyst precursor solutions are treated with molecular hydrogen for 1 h at 60°C before cyclohexene is added. However, in contrast to $(PPh_3)_2(CO)HRu(\mu\text{-}pz)_2Ir(TFB)$, the catalyst is recovered unchanged after the catalytic reactions, indicating that the diolefins coordinated to iridium atoms are not hydrogenated during the catalysis.

From studies on pyrazolato–iridium(I) complexes is known that the complex $[Ir(\mu\text{-}pz)(CO)(PPh_3)]_2$ reacts with molecular hydrogen to give $[IrH(pz)(CO)(PPh_3)]_2$

[85]. Thus, it is likely that during the induction period related diiridium species of the formula $Ir_2H_2pz_2(TFB)_2$ could be formed. Possibly an equilibrium as shown in Eq. (24) is reached:

$$[Ir(\mu\text{-}pz)(TFB)]_2 + H_2 \rightleftharpoons Ir_2H_2(pz)_2(TFB)_2 \quad (24)$$

In agreement with the equilibrium shown in Eq. (24), the kinetic study of the reduction of cyclohexene, in the presence of the dimer $[Ir(\mu\text{-}pz)(TFB)]_2$, indicates that the reaction rate is second order with regard to the hydrogen pressure. The experimental data fit a rate expression of the form:

$$\frac{-\,d[\text{cyclohexene}]}{dt} = k_{25}[\text{catalyst}]\ (P(H_2))^2 \quad (25)$$

The first-order dependence of the rate on the concentration of $[Ir(\mu\text{-}pz)(TFB)]_2$ suggests that the full catalytic cycle involves dinuclear species. Indeed, the non-dependence of the rate on the concentration of cyclohexene indicates that the olefin is not involved in the rate-determining step of the catalytic cycle or in a step previous to this. Therefore, the reaction of the catalyst with molecular hydrogen must be the initial step in the cycle. In light of these considerations, the following set of reactions has been proposed for the catalytic cycle [67]:

$$Ir_2H_2(pz)_2(TFB)_2 + H_2 \rightarrow Ir_2H_4(pz)_2(TFB)_2 \text{ (slow)} \quad (26)$$

$$Ir_2H_4(pz)_2(TFB)_2 + C_6H_{10} \rightarrow Ir_2H_2(pz)_2(TFB)_2 + C_6H_{12} \text{ (fast)} \quad (27)$$

2.6.3. Addition of silanes to olefins and terminal alkynes

In the presence of the five-coordinate chloro complex $IrCl(TFB)(AsPh_3)(PPh_3)$, 1-hexene reacts with triethylsilane to give hexane, 1-hexyl(triethyl)silane and three different hexenyl(triethyl)silanes. The relative amount of hexane formed is very similar to that corresponding to the hexenyl(triethyl)silanes. This has been rationalised in terms of a dehydrogenative silylation (Eq. (28)), which is competitive with a normal hydrosilylation (Eq. (29)) [86]:

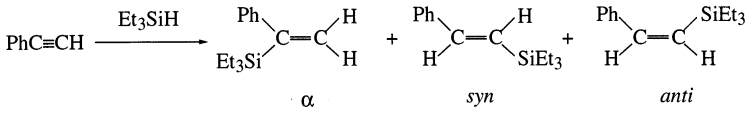
$$2C_6H_{12} + HSiEt_3 \rightarrow C_6H_{11}SiEt_3 + C_6H_{14} \quad (28)$$

$$C_6H_{12} + HSiEt_3 \rightarrow C_6H_{13}SiEt_3 \quad (29)$$

Interestingly, variations in the 1-hexene:triethylsilane ratio of 1:1, 3:1 and 6:1 cause a change in the ratio $C_6H_{11}SiEt_3$:$C_6H_{13}SiEt_3$ to 2.4:1, 4.8:1 and 8:1, respectively. A similar behaviour has been found for several rhodium catalysts [87].

In the presence of the dihydrido–silyl complexes $IrH_2(SiEt_3)(TFB)(PR_3)$ (PR_3 = PPh_3, PCy_3, P^iPr_3) [33] and the square–planar derivatives $[Ir(TFB)\{\kappa^2\text{-}{}^iPr_2PCH_2CH_2L\}]BF_4$ (L = OMe, NMe_2) [88] and $Ir(C_2Ph)(TFB)(PCy_3)$ [38], phenylacetylene undergoes reactions with triethylsilane. In all the cases, $PhCH{=}CH_2$, $PhC{\equiv}CSiEt_3$, *cis*-$PhCH{=}CH(SiEt_3)$, *trans*-$PhCH{=}CH(SiEt_3)$ and $Ph(SiEt_3)C{=}CH_2$ are formed. The amount of $PhCH{=}CH_2$ obtained is very similar to that of $PhC{\equiv}C(SiEt_3)$. As for 1-hexene, this is rationalised in terms of a dehydrogenative silylation (Eq. (30)), along with a normal hydrolsilylation (Eq. 31):

$$2PhC{\equiv}CH + HSiEt_3 \rightarrow PhCH{=}CH_2 + PhC{\equiv}CSiEt_3 \quad (30)$$



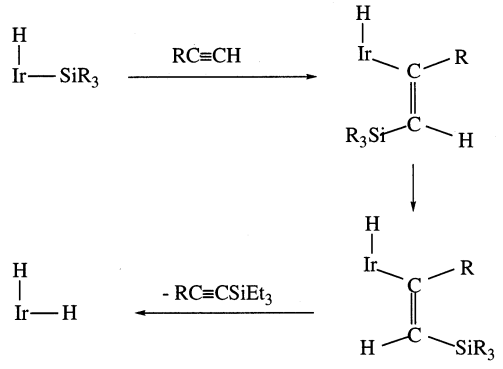
(31)

The major product in almost all cases is *cis*-PhCH=CH($SiEt_3$). The formation of this product is interesting because the *cis*-isomer is a result of the *trans*-addition of the silane to the alkyne. From a mechanistic point of view, it has been proposed that the *anti*-addition product is formed when the reaction involves the intervention of a radical-like species as an intermediate or transition state [89]. Non-radical pathways have also been reported. Dickers et al. [90] have found a *trans* to *cis* isomerization in the addition of triethylsilane to 1-hexyne catalysed by $RhCl(PPh_3)_3$. Brady and Nile [91] have reported that, in the presence of some phosphine–rhodium(I) complexes, the hydrosilylation of 1-pentyne with triethylsilane affords the *cis* product as the major species. They proposed a mechanism involving an initial insertion of the alkyne into the Rh–H bond of a Et_3Si–Rh–H intermediate to give Et_3Si–Rh{(*E*)-CH=CHR} species, which isomerizes to Et_3Si–Rh{(*Z*)-CH=CHR} via a zwitterionic carbene complex. The subsequent reductive elimination of the *anti*-addition product regenerates the catalyst.

In 1990, Ojima et al. [92] found that the addition of triethylsilane to 1-hexyne gives *cis*-1-(triethylsilyl)-1-hexene (major), *trans*-1-(triethylsilyl)-1-hexene (minor) and 2-(triethylsilyl)-1-hexene (minor) as reaction products. The proposed mechanism for the formation of the *anti*-addition product includes the insertion of the alkyne into the silicon–rhodium bond in the first place to form a (*Z*)-1-silyl-1-alkene-2-yl-Rh intermediate, instead of the previously proposed insertion into the Rh–H bond. Thus, this intermediate undergoes isomerization to the sterically more favoured (*E*)-1-silyl-alkene-2-yl-Rh complex, via a zwitterionic carbene compound, which is somewhat similar to the mechanism proposed by Brady and Nile.

We have observed that the complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os [93], Ru [94]) catalyse the addition of triethylsilane to phenylacetylene to afford predominant *anti*-addition of the silane to the alkyne. On the basis of spectroscopic studies, we proposed that the formation of *cis*-PhCH=CH($SiEt_3$) involves the insertion of the phenylacetylene into the M–Si bond of the intermediates $M(SiEt_3)Cl(CO)(P^iPr_3)_2$ (M = Os, Ru) followed by the isomerization of the resulting (*Z*)-silylvinyl derivatives to the *E* isomers, in line with the proposal of Ojima et al. [92].

Jun and Crabtree have examined the hydrosilylation of terminal alkynes in the presence of the complex $[IrH(H_2O)(bq)(PPh_3)_2][SbF_6]$ (bq = 7,8-benzoquinolinato) [95]. These reactions, in contrast with those catalysed by $MHCl(CO)(P^iPr_3)_2$ (M = Os, Ru) furthermore lead to $RC{\equiv}CSiR_3$. The proposed mechanism for the formation of this product involves the formation of an (*E*)-silylalkenyl intermediate, which undergoes a β-elimination process of the *endo*-hydrogen atom of the silylalkenyl group (Scheme 24). However, the participation of alkynyl–metal com-

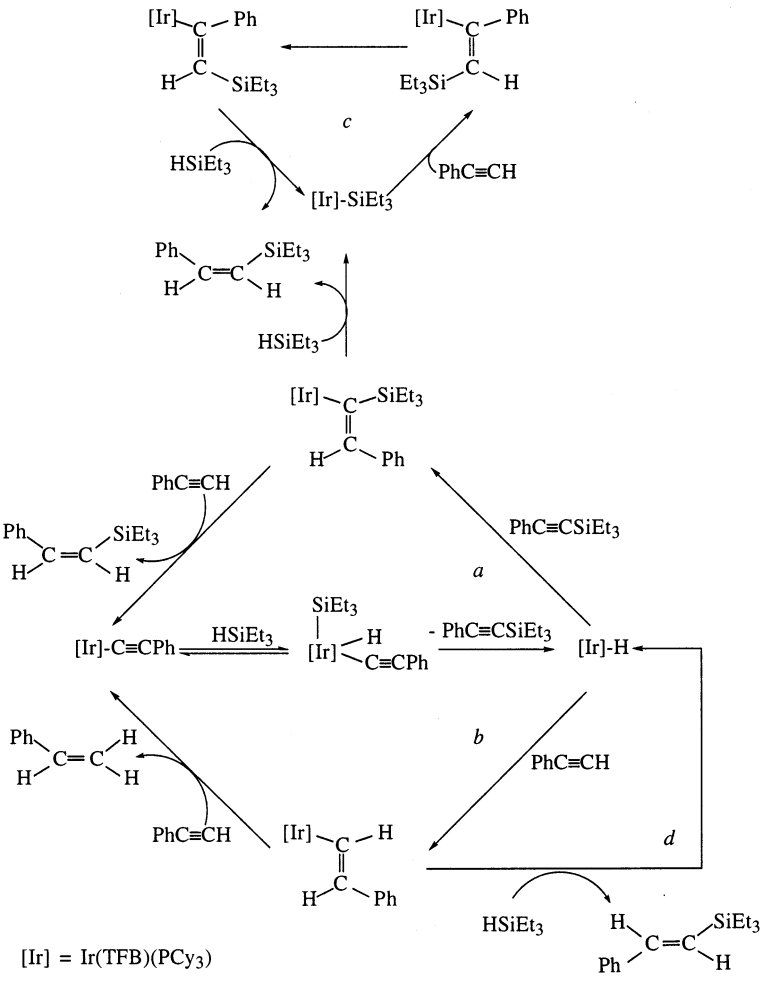


Scheme 24.

plexes as key intermediates for the formation of *cis*-RCH=CH($SiEt_3$) and RC≡C$SiEt_3$ should not be excluded. In this context, it has been found that the formation of the dehydrogenative silylation product takes place when the *cis*-alkenyl silane is the major product of the catalytic reaction [96]. Interestingly, in these cases, the catalysts are alkynyl derivatives or complexes which react with terminal alkynes to give alkynyl compounds [97]. A detailed study of the addition of triethylsilane to phenylacetylene in the presence of the alkynyl complex Ir(C_2Ph)(TFB)(PCy_3) has provided strong evidence in favour of this [38].

As has been previously mentioned in the presence of Ir(C_2Ph)(TFB)(PCy_3) PhCH=CH_2, PhC≡C$SiEt_3$, *cis*-PhCH=CH($SiEt_3$), *trans*-PhC=CH($SiEt_3$) and Ph($SiEt_3$)CH=CH_2 are obtained from the reaction. The relative amounts of each reaction product depend on the initial concentrations of phenylacetylene and triethylsilane. In the presence of 0.24 M of triethylsilane, the concentration of *trans*-PhCH=CH($SiEt_3$) is between 0.03 and 0.04 M and only traces of Ph($SiEt_3$)C=CH_2 are formed. Under these conditions, the amount of *cis*-PhCH=CH($SiEt_3$) decreases as the phenylacetylene concentration increases. Contrary to this behaviour, the amount of PhC≡C$SiEt_3$ rises. Scheme 25 illustrates different reaction sequences that allow us to rationalise these results.

The fact that the quantity of *trans*-PhCH=CH($SiEt_3$) formed is independent of the phenylacetylene concentration, and that the decrease of the amount of *cis*-PhCH=CH($SiEt_3$) is similar to the increase of the amount of PhC≡C$SiEt_3$, suggests that the formation of the *syn*-addition product is independent of the formation of *cis*-PhCH=CH($SiEt_3$) and PhC≡C$SiEt_3$ and, furthermore, suggests that the reaction pathways to afford the *anti*-addition product and PhC≡C$SiEt_3$ have some common point, which is sensitive to changes in the phenylacetylene concentration. According to Scheme 11, the dehydrogenative silylation product can be formed by reductive elimination from the alkynyl–hydrido–silyl intermediate IrH(C_2Ph)($SiEt_3$)(TFB)(PCy_3). The reductive elimination should afford IrH(TFB)(PCy_3), which could insert PhC≡C$SiEt_3$ (path *a*) to give an Ir{(CSiEt)=CHPh} alkenyl intermediate, or alternatively could react with phenyl-



Scheme 25.

acetylene to give a styryl derivative (path *b*). At higher phenylacetylene concentrations, both the silylalkenyl and the styryl species could afford the corresponding olefins and $Ir(C_2Ph)(TFB)(PCy_3)$. The formation of olefins and alkynyl compounds by reaction of alkenyl complexes and terminal alkynes is a well-known process [98]. Because paths *a* and *b* are competitive and path *b* would be favoured with the increase of the phenylacetylene concentration, the increase of this produces an increase in the amount of $PhC{\equiv}CSiEt_3$ and a decrease in the amount of *cis*-$PhCH{=}CH(SiEt_3)$.

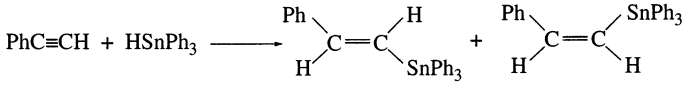
As an alternative to the reaction of the $Ir\{C(SiEt_3){=}CHPh\}$ intermediate with phenylacetylene to give $Ir(C_2Ph)(TFB)(PCy_3)$, this intermediate could also react with triethylsilane to give an $Ir{-}SiEt_3$ intermediate, which could yield the *anti*-addi-

tion product by Ojima's mechanism (path *c*). This reaction pathway should be favoured at high triethylsilane concentrations and would produce a decrease in the amount of $PhC{\equiv}CSiEt_3$. Experimental data show that the amount of the dehydrogenative silylation product decreases as the triethylsilane concentration rises. However, the amount of *anti*-addition product also decreases. This decrease in the amount of *cis*-$PhCH{=}CH(SiEt_3)$ on increasing the triethylsilane concentration is accompanied by an increase in the amount of *trans*-$PhCH{=}CH(SiEt_3)$ formed. According to the Chalk–Harrod mechanism [99], the *syn*-addition product could be formed by reaction of the styryl intermediate $Ir(CH{=}CHPh)(TFB)(PCy_3)$ with triethylsilane (path *d*), and its increase should involve a combined decrease of the amounts of $PhC{\equiv}CSiEt_3$ and *cis*-$PhCH{=}CH(SiEt_3)$. Although experimentally this is observed, a decrease in the amount of *trans*-$PhCH{=}CH(SiEt_3)$ on increasing the phenylacetylene concentration should also be expected and, as it has been previously mentioned, this does not occur. Hence, although it cannot be rejected that some amount of *trans*-$PhCH{=}CH(SiEt_3)$ is formed by path *d* of Scheme 25, the contribution of this reaction pathway to the overall *trans*-$PhCH{=}CH(SiEt_3)$ is not significant. Thus, the *syn*-addition product should be formed by isomerization of *cis*-$PhCH{=}CH(SiEt_3)$. In fact, experimentally, it has been observed that at 60°C in the presence of $Ir(C_2Ph)(TFB)(PCy_3)$ and triethylsilane, a mixture of 47% *cis*-$PhCH{=}CH(SiEt_3)$ and 53% *trans*-$PhCH{=}CH(SiEt_3)$ is converted into 4% *cis*-$PhCH{=}CH(SiEt_3)$ and 96% *trans*-$PhCH{=}CH(SiEt_3)$.

In summary, the reaction pathways *a* and *c* explain the formation of *cis*-$PhCH{=}CH(SiEt_3)$ and the reaction pathway *b* rationalises the formation of $PhC{\equiv}C(SiEt_3)$. The *syn*-addition product, *trans*-$PhCH{=}CH(SiEt_3)$, is mainly formed by isomerizaton of its *cis*-isomer.

2.6.4. Addition of stannanes to terminal alkynes

At 60°C and in 1,2-dichloroethane as solvent, the dihydrido–stannyl complex $IrH_2(SnPh_3)(TFB)(PCy_3)$ catalyses the addition of triphenylstannane to phenylacetylene to afford *trans*-$PhCH{=}CH(SnPh_3)$ (85%) and *cis*-$PhCH{=}CH(SnPh_3)$ (15%) (Eq. 32). The formation of the dihydrogenative stannylation product, $PhCH{=}CH(SnPh_3)$, is not observed [29].



(32)

Under the same conditions, the alkynyl complex $IrH(C_2Ph)(SnPh_3)(TFB)(PCy_3)$ also catalyses the addition of triphenylstannane to phenylacetylene. However in this case, the major product is *cis*-$PhCH{=}CH(SnPh_3)$ (60%), suggesting that for the hydrostannylation of terminal alkynes, the presence of alkynyl complexes also plays a major role in the formation of the *anti*-addition product.

3. Rhodium tetrafluorobenzobarrelene chemistry

3.1. The starting materials for rhodium–diolefin chemistry

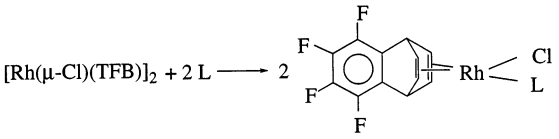
Dinuclear complexes of rhodium(I) of formula $[Rh(\mu\text{-}Cl)(diolefin)]_2$ (diolefin = 1,5-cycloctadiene, COD [1,100] or 2,5 norbornadiene, NBD [3]) are very easily obtained by reducing, in aqueous ethanol, rhodium trichloride hydrate in the presence of an excess of the corresponding diolefin 1,5-cycloctadiene, under refluxing conditions, or 2,5 norbornadiene, in the range 40–50°C. Interestingly, a microwave technique allows a rapid preparation of $[Rh(\mu\text{-}Cl)(COD)]_2$ [101].

The fluorinated barrelene diolefins, tetrafluorobenzobarrelene (TFB) and tri-*o*-tetra-methyltetrafluorobenzobarrelene (Me_xTFB, $x = 3$ or 4) react similarly with rhodium trichloride hydrate, in aqueous ethanol, to render the corresponding $[Rh(\mu\text{-}Cl)(TFB)]_2$ or $[Rh(\mu\text{-}Cl)(Me_xTFB)]_2$ complexes [9]. The reactions occur in about 1 h in boiling ethanol although several days are required if the mixture is stirred at r.t. All of them are obtained in high yields. Other interesting starting materials are the related $[Rh(\mu\text{-}OMe)(diolefin)]_2$ complexes, prepared by reacting $[Rh(\mu\text{-}Cl)(diolefin)]_2$ with potassium hydroxide in methanol [4]. The basicity of $[Rh(\mu\text{-}OMe)(diolefin)]_2$ has been frequently used for the preparation of other complexes [6]. The availability of the above mentioned dinuclear starting materials has promoted the development of an extensive and rich chemistry of neutral and cationic rhodium complexes [5,6], cycloctadiene and norbornadiene complexes being by far the most abundant. We will discuss below the related rhodium chemistry with tetrafluorobenzobarrelene ligands.

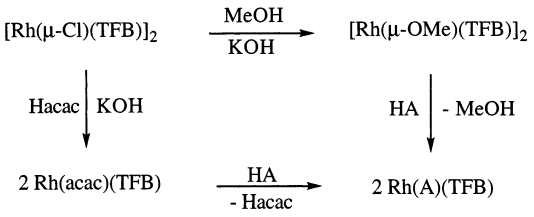
3.2. Neutral rhodium tetrafluorobenzobarrelene complexes

3.2.1. Mononuclear complexes

3.2.1.1. Mononuclear RhCl(TFB)L complexes. Bridge cleavage reactions of $[Rh(\mu\text{-}Cl)(TFB)]_2$ or $[Rh(\mu\text{-}Cl)(Me_xTFB)]_2$ ($x = 3$, 4) with stoichiometric amounts of triphenylphosphine yield mononuclear $RhCl(TFB)(PPh_3)$ and $RhCl(Me_xTFB)(PPh_3)$ complexes [9]. Similarly, the related RhCl(TFB)L compounds, where L = 4-amino-pyridine, 2-amino-pyridine, 4-cyano-pyridine, 2-cyano-pyridine [102], pyridazines, 4,6-bis(3,5-dimethylpyrazol-1-yl)pyridimine [103], 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole [104], 1,8-naphthyridine [105], benzotriazoles [106], tris(pyrazolyl)methane [24], 7-azaindole [107,108], 2,2′-dipyridylamine [109] and *N*,*N*′-diphenylbenzamidine [123], are obtained by reacting $[Rh(\mu\text{-}Cl)(TFB)]_2$ with L, according to Eq. 33:



(33)



Scheme 26.

Some of these RhCl(TFB)L complexes have been obtained in the course of preparative studies on di- and polynuclear rhodium complexes, because all the above mentioned nitrogen ligands present two or more nitrogen donor centres capable of coordination. The vast majority of the RhCl(TFB)L complexes are square–planar with only one coordinated nitrogen. However, five-coordinate compounds are obtained in some cases; thus, five coordination seems to be present in the RhCl(TFB)(NH_2bpt) complex (NH_2bpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole), although in solution an equilibrium is reached, between neutral five-coordinate and ionic square species, $[Rh(TFB)(NH_2bpt)]^+$, with ionic Cl^- [104], according to Eq. (34):

$$RhCl(TFB)(NH_2bpt) \rightleftharpoons [Rh(TFB)(NH_2bpt)]^+ + Cl^- \quad (34)$$

3.2.1.2. Mononuclear Rh(A)(TFB) complexes. Potential anionic bidentate chelating ligands (HA) react with $[Rh(\mu\text{-}Cl)(TFB)]_2$ or $[Rh(\mu\text{-}Cl)(Me_xTFB)]_2$, in the presence of potassium hydroxide or triethylamine, yielding mononuclear complexes of formula Rh(A)(Me_xTFB), where HA = acetylacetone [9], a variety of substituted tropolones, salicylaldehyde [110], 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 [111], 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole [104], 3,5-bis(pyridin-2-yl)-1,2,4-triazole [112], 5,7-dimethyl-1,8-naphthyridine-2-one [113]. In same cases, as for 2,2′-dipyridylamine, the deprotonation of the ligand was performed by using butyllithium [109]. Same Rh(A)(TFB) complexes have been also prepared by depronation, in basic media, of the coordinated neutral HA ligand from RhCl(TFB)(HA). Other useful synthetic strategies are based on the ability of ligands containing N–H bonds to abstract the methoxo or acetylacetonate groups from $[Rh(\mu\text{-}OMe)(TFB)]_2$ [4] or Rh(acac)(TFB) [9] compounds (Scheme 26).

On the other hand, Rh(Cp)(TFB) and Rh(Cp)(Me_xTFB) complexes are obtained by reacting the chloro-bridged dimers with lithium cyclopentadienyl [9].

3.2.2. Dinuclear complexes

3.2.2.1. Dinuclear {RhCl(TFB)}$_2$(L) complexes. The large majority of dinuclear complexes are obtained from the $[Rh(\mu\text{-}Cl)(TFB)]_2$ complex [9]. The reaction of some bidentate ligands (L^2), such as dipyridylamine [109], 4,6-bis(3,5-dimethylpyrazol-1-yl)pyridimine [103], 3,3′,5,5′-tetramethyl-4,4′-bypyrazole, 4,4′-methylen-bis(3,5-dimethylpyrazole [114] 1,6-bis(2′-benzimidazolyl)-2,5-dithiahexane [115] or

bis(pyrazolyl)methanes [116], with $[Rh(\mu\text{-}Cl)(TFB)]_2$ yield the dinuclear complexes of formula $\{RhCl(TFB)\}_2(L^2)$ [103]. However, the final products from the reaction of $[Rh(\mu\text{-}Cl)(diolefin)]_2$ with 3,5-bis(4-methylpyrazol-1-yl)-4-methylpyrazole (L^3) depends on the diolefin; thus a dinuclear $\{RhCl(TFB)\}_2(L^3)$ compound was obtained when the diolefin is tetrafluorobenzobarrelene, but a neutral mononuclear $Rh(Cl)(COD)(L^3)$ compound is formed when the diolefin is 1,5-cyclooctadiene [10]. A similar behaviour is also observed in the reaction of $CH_2(4\text{-}Brpz)_2$ with $[Rh(\mu\text{-}Cl)(diolefin)]_2$ dimers; analogously a dinuclear $\{RhCl(TFB)\}_2(CH_2(4\text{-}Brpz)_2)$ complex was isolated for diolefin = TFB, but a mononuclear $RhCl(COD)(CH_2(4\text{-}Brpz)_2)$ compound was formed for diolefin = COD [116]. It is interesting to mention the presence of an equilibrium in polar solvents (S) between dinuclear neutral and cationic species as observed for the bis(pyrazolyl)methane $CH_2(Rpz)_2$ complexes (Eq. (35)) [116]:

$$\{RhCl(TFB)\}_2(CH_2(Rpz)_2) \rightleftharpoons [\{Rh(TFB)S\}_2(CH_2(Rpz)_2)]^{2+} + 2Cl^- \quad (35)$$

The dinuclear $\{RhCl(TFB)\}_2(L^3)$ complex presents, in solution, a prototropic exchange in the central pyrazole of the 3,5-bis(4-methylpyrazol-1-yl)-4-methylpyrazole (L^3) ligand that is slowed down at low temperature [10].

3.2.2.2. Dinuclear $[Rh(\mu\text{-}L)(TFB)]_2$ complexes. The bridging chlorine atoms in the $[Rh(\mu\text{-}Cl)(TFB)]_2$ complex can be substituted with iodine or methoxo groups, by treatment with potassium iodide [9] or methanol in basic media [4,9].

A large variety of anionic binucleating ligands derived from azole type ligands (Haz) [117] allowed the preparation of dinuclear homovalent rhodium complexes of formula $[Rh(\mu\text{-}az)(TFB)]_2$. Some possible preparative routes are:

$$[Rh(\mu\text{-}Cl)(TFB)]_2 + Haz + NaOH \text{ (or } NEt_3) \rightarrow [Rh(\mu\text{-}az)(TFB)]_2 + NaCl \text{ (or } HNEt_3Cl) \quad (36)$$

$$2Rh(acac)(TFB) + 2Haz \rightarrow [Rh(\mu\text{-}az)(TFB)]_2 + 2Hacac \quad (37)$$

$$2[Rh(TFB)(Haz)_2]ClO_4 + 2KOH \rightarrow [Rh(\mu\text{-}az)(TFB)]_2 + KClO_4 + K(az) + 2H_2O \quad (38)$$

(Haz = pyrazole [118], indazole [119], benzotriazoles [106], 1,2,4-triazole [120], tetrazole [121]). These azolato complexes present flexible open-book structures as shown in Fig. 8 for the pyrazolato derivative.

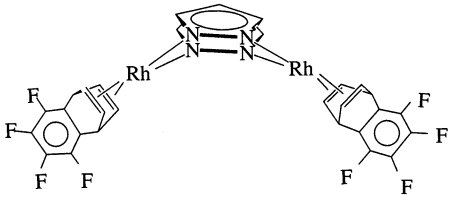


Fig. 8.

However complexes of higher nuclearity are obtained when imidazole (Him) or 2-methylimidazole are used. The tetrafluorobenzobarrele $[Rh(\mu\text{-im})(TFB)]_x$ complex is easily displaced by carbon monoxide to yield the tetranuclear $[Rh(\mu\text{-im})(CO)_2]_4$ complex [122] fully characterised by X-ray diffraction methods.

A heterobridged dinuclear complexes of formula $Rh_2(\mu\text{-ttz})(\mu\text{-}N_3)(TFB)_2$ containing tetrazolate (ttz) and azide bridging ligands, can be obtained by treating $[Rh(\mu\text{-Cl})(TFB)]_2$ with tetrazole, Rh(acac)(TFB) and NaN_3 [121]. Mixed dinuclear rhodium indazolato complexes of formula (TFB)Rh(μ-idz)Rh(COD) or (TFB)-Rh(μ-idz)Rh(CO)(PPh_3) have been prepared by reacting the cationic complex $[(TFB)Rh(Hidz)_2]ClO_2$ with Rh(acac)(COD) or Rh(acac)CO(PPh_3), in the presence of triethylamine [119].

Dinuclear rhodium complexes presenting an approximately face-to face disposition are prepared by using binucleating ligands containing N–C–X (X = N, O, S) units. The tetrafluorobenzobarrelene diolefin seems to favour dinuclear structures; thus, the dinuclear $[Rh\{\mu\text{-}CPh(NPh)_2\}(TFB)]_2$ complex is isolated by reacting $[Rh(\mu\text{-Cl})(TFB)]_2$ with *N*,*N*′-diphenylbenzamidine and potassium hydroxide, but a mononuclear complex of formula $Rh\{CPh(NPh)_2\}(COD)$ is obtained when the diolefin is 1,5-cyclooctadiene (Eq. (39)):

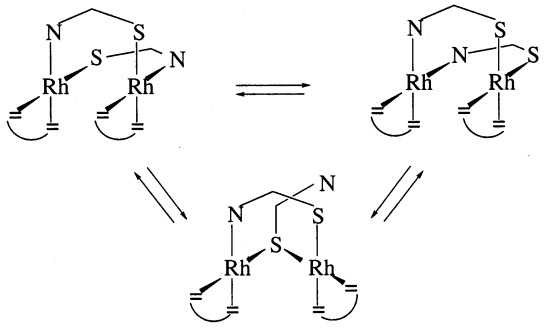
$$x/2[Rh(\mu\text{-Cl})(\text{diolefin})]_2 + x\,PhN{=}CPh{-}NHPh + x\,KOH \rightarrow [Rh(CPH\{NPh_2\}_2)(\text{diolefin})]_x + x\,KCl + x\,H_2O \quad (39)$$

diolefin = TFB, $x = 2$; diolefin = COD, $x = 1$.

Both benzamidinato diolefin rhodium complexes have been characterised by X-ray diffraction methods, confirming the dinuclear formulation of the tetrafluorobenzobarrelene complex, with two *N*,*N*′-diphenylbenzamidinate ligands bridging two rhodium atoms with an intermetallic distance of 2.982 Å [123]. Related dinuclear complexes of general formula $[Rh\{\mu\text{-}N,N'\text{-PhNPyR}\}(TFB)]_2$ are obtained by reaction of $[Rh(\mu\text{-Cl})(TFB)]_2$ with a solution of the lithium salt of 2-(N-anilino)-4-pyridine or 2-(N-anilino)-4-terbutylpyridine [124]. The analogous reaction with 7-azaindole (Haza) in the presence of potassium hydroxide gives $[Rh(\mu\text{-aza})(TFB)]_2$. This complex can be also obtained by removal of the pyrrole NH proton of the coordinated 7-azaindole ligand in the mononuclear RhCl(TFB)(Haza) complex. A dinuclear unsymmetrical complex of formula $(TFB)Rh(\mu\text{-aza})_2Rh(CO)_2$ is obtained by reaction of $[Rh(\mu\text{-aza})(TFB)]_2$. with its carbonyl derivative $[Rh(\mu\text{-aza})(CO)_2]_2$ [107,108].

$[Rh(\mu\text{-Cl})(TFB)]_2$ reacts with an equimolecular mixtures of potassium hydroxide and 2-hydroxypyridine or 1,8-naphthyridine-2-one (HOnapy) to give $[Rh(\mu\text{-Opy})(TFB)]_2$ [125] or $[Rh(\mu\text{-Onapy})(TFB)]_2$ [113,126]. The later complex can be alternatively obtained by addition of 1,8-naphthyridine-2-one to $[Rh(\mu\text{-OMe})(TFB)]_2$ solutions. As previously observed in benzamidinato diolefin rhodium complexes, whilst the tetrafluorobenzobarrele complex $[Rh(\mu\text{-Onapy})(TFB)]_2$ is dinuclear the cyclooctadiene compound Rh(Onapy)(COD) is mononuclear.

Reaction of $[Rh(\mu\text{-}Cl)(TFB)]_2$ with lithium pyridin-2-thiolato or lithium benzothiazole-2-thiolato, affords the dinuclear complexes $[Rh(\mu\text{-}SC_5H_4N)(TFB)]_2$ and $[Rh(\mu\text{-}C_7H_4NS_2)(TFB)]_2$. The pyridin-2-thiolato complex shows fluxional behaviour in solution associated with the bridging ligand (Eq. 40).



(40)

Interestingly, the molecular structure of the tetrafluorobenzobarrelene complex shows one of the pyridin-2-thiolato group acting as a bridge, whereas the other pyridin-2-thiolato ligand bridges through the sulfur atom only [127,128].

Rh(acac)(TFB) [9] reacts with a stoichiometric amount of diphenylphosphine sulfide ($Ph_2P(S)H$) to give $[Rh(\mu\text{-}SPPh_2)(TFB)]_2$. The crystal structure of the related $[Rh(\mu\text{-}SPPh_2)(COD)]_2$ complex confirms a dimeric structure in which two $SPPh_2^-$ ligands bridge the metal atoms through their S and P donor atoms [129]. The related heterobridged $Rh_2(\mu\text{-}SPPh_2)(\mu\text{-}Cl)(TFB)_2$ complex, containing one chloride anion and one thiophosphinito group as bridging ligands, has been synthesised by a redistribution reaction of the homobridged compounds $[Rh(\mu\text{-}SPPh_2)(TFB)]_2$ and $[Rh(\mu\text{-}Cl)(TFB)]_2$, according to Eq. (41) [130]:

$$[Rh(\mu\text{-}SPPh_2)(TFB)]_2 + [Rh(\mu\text{-}Cl)(TFB)]_2 \rightarrow 2\ Rh_2(\mu\text{-}SPPh_2)(\mu\text{-}Cl)(TFB)_2 \quad (41)$$

The dinuclear $[Rh(\mu\text{-}SPh)(TFB)]_2$ complex can be isolated in almost quantitative yield by treating $[Rh(\mu\text{-}Cl)(TFB)]_2$ with the lithium salt of thiophenol [131].

3.2.2.3. Dinuclear $Rh_2(\mu\text{-}L)(TFB)_2$ complexes. The reaction of 2 mol of Rh(acac)(TFB) with 1 mol of oxalic acid leads to the formation of the dinuclear $Rh_2(\mu\text{-}C_2O_4)(TFB)_2$ complex. A related $(TFB)Rh(\mu\text{-}C_2O_4)Rh(COD)$ complex can be obtained by reaction of the $Rh(HC_2O_4)(COD)$ compound, prepared by treating Rh(acac)(COD) with a stoichiometric amount of oxalic acid, with Rh(acac)(TFB). In these complexes, the dicarboxylate anion functions as a tetradentate ligand capable of bidentating the two metals simultaneously [132].

The treatment of $[Rh(\mu\text{-}OMe)(TFB)]_2$ [4] with chloranilic acid (H_2CA) or 2,5-dihydroxy-1,4-benzoquinone (H_2DHBQ) in 1:1 ratio gives the dinuclear complexes $Rh_2(\mu\text{-}CA)(TFB)_2$ (Fig. 9) and $Rh_2(\mu\text{-}DHBQ)(TFB)_2$ [133]. In these complexes the CA^{2-} and $DHBQ^{2-}$ dianions in the *p*-quinone form, chelate the two rhodium(I) atoms through the oxygen atoms. The dianions are planar and behave as tetradentate bis-chelating ligands resembling those shown by the oxalate dianion.

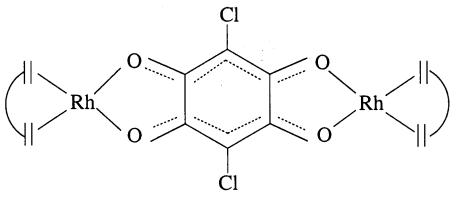
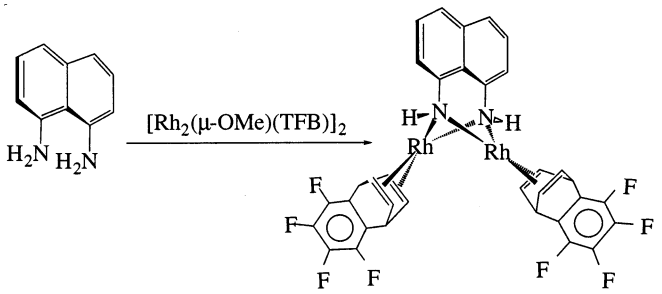


Fig. 9.

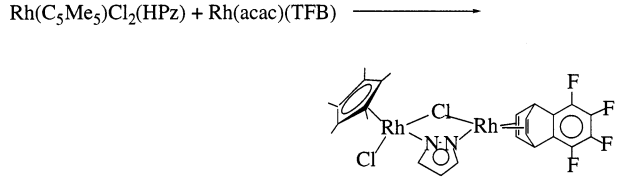
The reaction of $[Rh(\mu\text{-OMe})(TFB)]_2$ [4] with stoichiometric amounts of 1,8-diaminonaphthalene causes partial deprotonation of the ligand and formation of the di-μ-amido dirhodium complex of formula $Rh_2\{\mu\text{-}1.8\text{-}(NH)_2C_{10}H_6\}(TFB)_2$ [134], according to Eq. 42:



(42)

The two amide centres are bound to the two rhodium atoms in both a bridging, and a chelating manner, as substantiated by the X-ray structural characterisation of the derived $Rh_2\{\{\mu\text{-}1.8\text{-}(NH)C_{10}H_6\}(CO)_4$ complex, easily prepared by displacing the coordinated diolefin by carbon monoxide [135]. Interestingly, this dinuclear tetrafluorobenzobarrelene complex undergoes two sequential one-electron oxidations at a platinum bead electrode [134].

3.2.2.4. Heterodinuclear and heterovalent complexes. A general synthetic strategy for the preparation of heterodinuclear or heterovalent complexes, involves the reaction of the tetrafluorobenzobarrelene derivatives M(acac)(TFB) (M = Rh or Ir) or $[Rh(\mu\text{-OMe})(TFB)]_2$, with mononuclear complexes of formula $LM'Cl_2(HL')$ (M′ = Rh or Ir, L = C_5Me_5; M′ = Ru, L = *p*-cymene; HL′ = pyrazole, diphenylphosphine). The latter compounds can be prepared by cleavage of the $[LM'Cl]_2$ dimers with HL′ [136]. Thus, the reaction of the mononuclear pyrazole compound $Rh(C_5Me_5)Cl_2(HPz)$ with Rh(acac)(TFB), leads to the formation of the heterovalent complex $(C_5Me_5)ClRh(\mu\text{-}Cl)(\mu\text{-}Pz)Rh(TFB)$ [137] according to Eq. 43:



(43)

The X-ray structure shows this heterobridged complex is composed of two rhodium atoms, Rh(III) and Rh(I), bridged by a chlorine atom and a pyrazolate group.

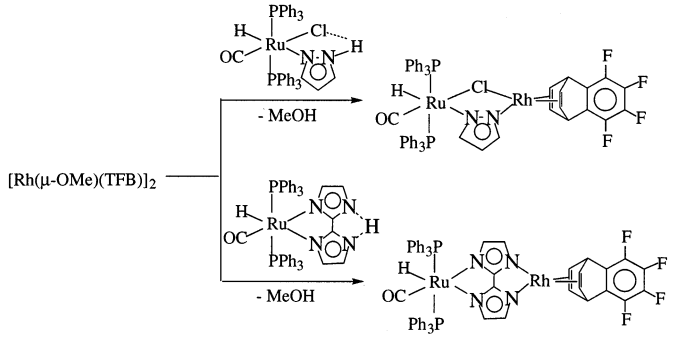
Similarly, the reaction of $LM'Cl_2(HPz)$ ($M' = Ru$, L = p-cymene; $M = Rh$ or Ir, $L = C_5Me_5$) complexes [136] with M(acac)(TFB) (M = Rh or Ir) derivatives leads to heterodinuclear complexes of general formula $LM'Cl_2(Pz)M(TFB)$ [138]. The X-ray structure of (*p*-cymene)Ru(μ-Cl)$_2$(μ-Pz)Rh(TFB) shows a triple-bridged formulation in contrast with the double-bridged formulation observed for the isoelectronic $(C_5Me_5)ClRh(\mu\text{-}Cl)(\mu\text{-}Pz)Rh(TFB)$ [137].

Heterovalent and heteronuclear diphenylphosphido-bridged complexes of formula $LM'Cl_2(\mu\text{-}PPh_2)Rh(TFB)$ can be prepared by reaction of $LM'Cl_2(HPPh_2)$ ($M = Ru$, L = *p*-cymene; $M = Rh$, $L = C_5Me_5$) complexes with $[Rh(\mu\text{-}OMe)(TFB)]_2$ [139a].

On the other hand, the well known acetylacetonato complexes $M(C_5Me_5)(acac)Cl$ (M = Rh, Ir) [136] also provide a preparative route to heterovalent and heteronuclear complexes. Thus, these acetylacetonato complexes react with $[Rh(TFB)(HPz)_2]^+$, in the presence of KOH to give $(C_5Me_5)ClM(Pz)_2Rh(TFB)$ compounds [137,138]. The heterovalent dirhodium complex, $(C_5Me_5)ClRh(Pz)_2Rh(TFB)$, can also be prepared by treating RhCl(TFB)(HPz) with $Rh(C_5Me_5)(acac)(Pz)$. The latter mononuclear complex also reacts with $[Rh(TFB)(HPz)_2]^+$, in the presence of KOH, to yield $(C_5Me_5)(Pz)Rh(Pz)_2Rh(TFB)$ [137].

A family of heterodinuclear hydrido–ruthenium–rhodium complexes containing bridging pyrazolate (Pz) or 2,2′-biimidazolate (Bim) ligands of formula $(PPh_3)_2(CO)HRu(\mu\text{-}Cl)(\mu\text{-}Pz)Rh(TFB)$ or $(PPh_3)_2(CO)HRu(\mu\text{-}Bim)Rh(TFB)$ can be prepared by reaction of mononuclear hydrido ruthenium complexes, $RuHCl(CO)(HPz)(PPh_3)_2$ or $RuH(CO)(HBim)(PPh_3)_2$, with $[Rh(\mu\text{-}OMe)(TFB)]_2$ [22,61] (Scheme 27).

The heterodinuclear osmium–rhodium complex $[(CO)_2(P^iPr_3)_2Os(\mu\text{-}H)(\mu\text{-}Pz)Rh(TFB)]BF_4$ containing bridging hydride and pyrazolate groups (Fig. 10) has



Scheme 27.

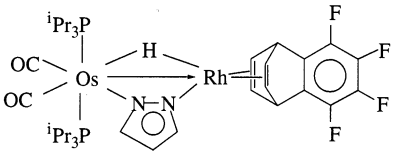


Fig. 10.

been prepared by reacting $[OsH(CO)_2(HPz)(P^iPr_3)_2]BF_4$ with $Rh(\mu\text{-}OMe)(TFB)]_2$ [139b]. The presence of a dative Os–Rh bond has been proposed.

The heteronuclear cobalt–rhodium tetraflorobenzobarrelene complex, (C_5Me_5)-$Co\{P(O)(OC_2H_5)_2\}_3Rh(TFB)$, has been prepared by the reaction of the oxygen tripod ligand $[(C_5Me_5)Co\{P(O)(OC_2H_5)_2\}_2]^-$ with $[Rh(\mu\text{-}Cl)(TFB)]_2$. The resulting complex contains a five-coordinated rhodium centre and presents fluxional behaviour [140].

3.2.3. Tri- tetra- and other polynuclear complexes

The trinuclear heterobridged complex $PdRh_2(\mu\text{-}Pz)_2(\mu\text{-}Cl)(TFB)_2$, containing chloride and pyrazolate as bridging ligands, can be obtained by reacting $PdCl_2(HPz)_2$ with Rh(acac)(TFB). This heterotrinuclear complex reacts with potassium pyrazolate to yield the homobridged $PdRh_2(\mu\text{-}Pz)_4(TFB)_2$ complex, containing four pyrazolate anions as bridging ligands (Fig. 11). The molecular structure of the carbonyl derivative $PdRh_2(\mu\text{-}Pz)_4(CO)_4$ confirms the proposed formulation with an intermetallic palladium–rhodium distance of 3.578 Å [141].

The above mentioned dirhodium tetrazolate or triazolate complexes still have uncoordinated nitrogen atoms and therefore, can act as donor centres for the construction of compounds of higher nuclearity. Thus, the addition of the appropriate amounts of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ to $[Rh(\mu\text{-}az)(TFB)]_2$ (az = ttz, tz) or $Rh_2(\mu\text{-}ttz)(\mu\text{-}N_3)(TFB)_2$ give trinuclear $Rh_3(\mu_3\text{-}az)(\mu\text{-}X)Cl(TFB)(CO)_4$ (X = Cl, N_3) (Fig. 12) [120,121]. The related azide complex $Rh_3(\mu_3\text{-}tz)(\mu\text{-}N_3)(N_3)(TFB)(CO)_4$ can be prepared by reacting $[Rh(\mu\text{-}N_3)(CO)_2]_2$ to $[Rh(\mu\text{-}tz)(TFB)]_2$. [120].

In general, these trinuclear complexes show metallic lustre and marked dichroism, suggesting metal–metal interactions which were confirmed by the X-ray determinations of $Rh_3(\mu_3\text{-}tz)(\mu\text{-}Cl)Cl(TFB)(CO)_4$. This complex shows a stacking arrangement of centred rhodium units with an intermetallic separation of 3.425 Å

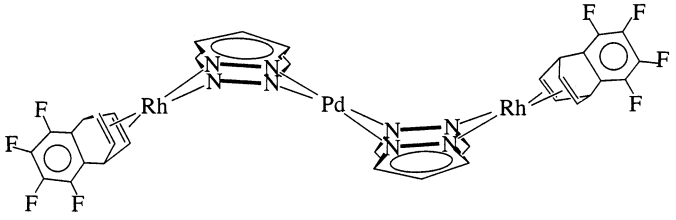


Fig. 11.

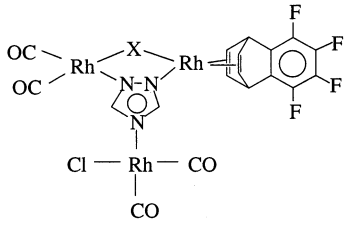


Fig. 12.

[120]. The related benzotriazolate (btz) dirhodium complexes also have two uncoordinated nitrogen atoms potentially available for the construction of tetranuclear complexes. Thus, tetranuclear complexes of formula $Rh_4(\mu_3\text{-btz})_2Cl_2(TFB)_2(COD)_2$ can be prepared by treating $[Rh(\mu\text{-btz})(diolefin)]_2$ (diolefin = TFB, COD) with $[Rh(\mu\text{-Cl})(diolefin)]_2$ (diolefin′ = COD, TFB) [106].

A heterovalent tetranuclear bimidazolate (bim) complex of formula $[(C_5Me_5)ClRh(bim)Rh(TFB)]_2$ is obtained by reacting $Rh(C_5Me_5)Cl(Hbim)$ with Rh(acac)(TFB). This complex contain two bim^{2-} anion coordinating the rhodium atoms in oxidation states, III and I, in a tetradentate manner [142]. Dinuclear $\{RhCl(TFB)\}_2(L^2)$ complexes containing ligands with acidic hydrogens such as 1,6-bis(2′-benzimidazolyl)-2,5-dithiahexane [115] or 3,3′,5,5′-tetramethyl-4,4′-bypyrazole [114] react with triethylamine to yield tetra- or octanuclear complexes [114,115].

Several tetranuclear complexes derived from polydentate anionic ligands containing N and S donor atoms have been reported. Thus, the reaction of 2,6-dimercaptopyridine, $Py(SH)_2$ with $[Rh(\mu\text{-OMe})(diolefin)]_2$ (diolefin = TFB, COD) in a molar ratio 1:1 gives tetranuclear $Rh_4(\mu\text{-}PyS_2)_2(diolefin)_4$ complexes (Fig. 13).

The tetranuclear formulation was conclusively determined by the X-ray analysis of $Rh_4(\mu\text{-}PyS_2)_2(COD)_4$. These complexes present two tridentate 2,6-dimercaptopyridine ligands bridging all of the four rhodium atoms, in such a way that one of the S atoms of each bridging ligand is bonded to one metal while the second one is coordinated to two different rhodium centres [143]. Tetranuclear complexes of formula $Rh_4(\mu\text{-HBzimt})_2Cl_2(diolefin)_4$ were prepared by reacting $RhCl(H_2Bzimt)(diolefin)$ (H_2Bzimt = 2-mercaptobenzimidazole; diolefin = TFB, COD) with $[Rh(\mu\text{-Cl})(diolefin)]_2$. In solution the cyclooctadiene derivative shows

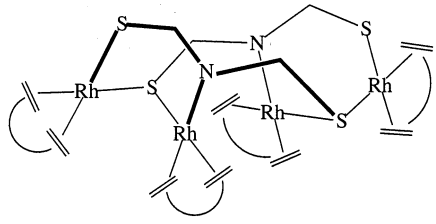


Fig. 13.

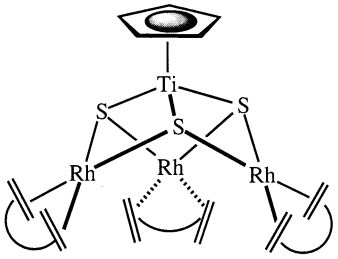


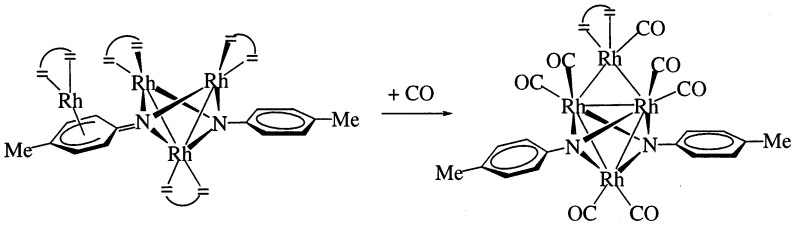
Fig. 14.

two species, due to a linkage isomerization, whilst the tetrafluorobenzobarrene compound exists as a single isomer in solution [144].

A tetranuclear complex of formula $Rh_4(SPPh_2)_6(TFB)_2$ has been isolated by reaction of Rh(acac)(TFB) with the dinuclear $Rh_2(SPPh)_4(SPHPh)_2$ complex, previously obtained by treatment of $Rh_2(O_2CMe)_4(MeOH)_2$ with $Ph_2P(S)H$, showing the flexibility of the thiophosphinite ligand [129].

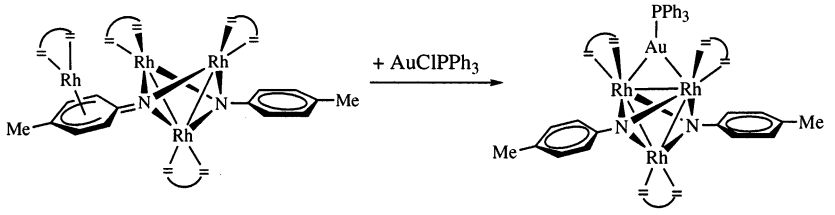
An early–late heterometallic complex of formula $(C_5H_5)Ti(\mu_3\text{-}S)_3\{Rh(TFB)\}_3$ has been prepared by reacting $(C_5H_5)_2Ti(SH)_2$ with $[Rh(\mu\text{-}OMe)(TFB)]_2$ and its X-ray structure shows an incomplete distorted cubane-type structure involving the four metals and the three triple-bridging sulfur atoms. The titanium atom presents the usual pseudotetrahedral coordination whilst the three rhodium centres are in distorted square–planar environments (Fig. 14) [145].

An unusual tetrarhodium complex containing imido ligands has been recently reported by reacting $[Rh(\mu\text{-}Cl)(TFB)]_2$ with *p*-toluidine and butyllithium. This novel $Rh_4(\mu\text{-}p\text{-}MeC_6H_4N)_2(TFB)_4$ complex possesses a triangular metal core with one nonbonded edge and a fourth metal atom η^5-coordinated to one arene ring [146]. It reacts with carbon monoxide, according to Eq. 44, to yield $Rh_4(\mu\text{-}p\text{-}MeC_6H_4N)_2(TFB)(CO)_7$ that has also been characterised by X-ray diffraction:



(44)

Its structure consists of an essentially planar butterfly arrangement of the metal atoms in which two triangles of Rh atoms share a common edge. This metal mobility involves the unprecedented formation of three new Rh–Rh bonds [147]. The $Rh_4(\mu\text{-}p\text{-}MeC_6H_4N)_2(TFB)_4$ complex reacts with $AuCl(PPh_3)$ to give the heterometallic cluster $Rh_3(\mu\text{-}p\text{-}MeC_6H_4N)_2(TFB)_3Au(PPh_3)$ according to Eq. 45 [148]:



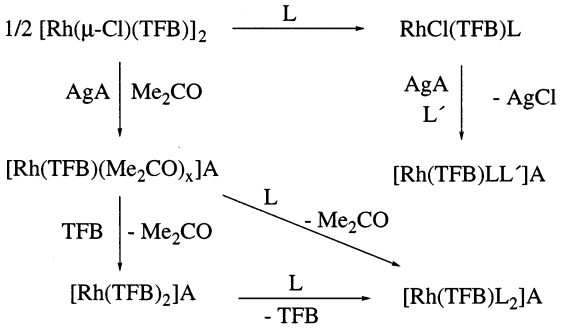
(45)

Heterometallic clusters of higher nuclearity are easily prepared by reacting some carbonyl derivatives with HgI_2 or $PdCl_2(NCPh)_2$ to give $\{Rh_3(\mu\text{-}p\text{-}MeC_6H_4N)_2(CO)_6\}_2Hg$ or $\{Rh_3(\mu\text{-}p\text{-}MeC_6H_4N)_2(CO)_6\}_2Pd(CO)(NCPh)$. The latter complex has been characterised by X-ray methods showing a planar raft-like arrangement of the seven metal atoms [148].

3.3. Cationic rhodium tetrafluorobenzobarrelene complexes

3.3.1. Mononuclear complexes

The addition of $AgClO_4$ to $[Rh(\mu\text{-}Cl)(TFB)]_2$, in acetone solution, leads to the formation of a non-isolable $[Rh(TFB)(Me_2CO)_x]ClO_4$ intermediate. The solvated acetone can be displaced by tetrafluorobenzobarrelene and other monodentate or bidentate ligands to yield $[Rh(TFB)_2]ClO_4$, $[Rh(TFB)L_2]ClO_4$ or $[Rh(TFB)(L–L)]ClO_4$ complexes [149]. Other silver salts such as $AgBF_4$ or $AgPF_6$ can alternatively be used. The addition of 2 mol of the monodentate ligands, or 1 mol of the bidentate ligand, to solutions of $[Rh(TFB)_2]^+$ leads to the displacement of one of the tetrafluorobenzobarrelene ligands to yield to cationic $[Rh(TFB)L_2]^+$ or $[Rh(TFB)(L–L)]^+$ species. Ionic species are also formed by adding donor ligands to $[Rh(\mu\text{-}Cl)(TFB)]_2$ and upon sodium or ammonium salts of BF_4^-, PF_6^-, BPh_4^-, or ClO_4^- and subsequent working up the cationic complexes can be easily isolated. Following the above mentioned methods (Scheme 28) a variety of cationic tetrafluorobenzobarrelene complexes with neutral, L or L–L, ligands have been prepared; L = pyridines [102,150], nitriles, aniline [150], pyrazole, imidazoles [151], indazole [119], tertiary phosphines [150], triphenylarsine, triphenylstibine [149],



Scheme 28.

dimethylsulfoxide and tetrahydrothiophen [152,1]; L–L = 2,2′-bipyridine, phenanthroline, diamines, 8-aminoquinoline, 2,2′-diquinolyl, diphosphines [150], 2,2′-biimidazole, 2,2′-bibenzimidazole [151], 2-2′dipyridilamine [109], bis(pyrazolyl)methane [116], 3,5-bis(pyridin-2-yl)-1,2,4-triazole [112], 2-2′dipyridilamine, 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole [104], pyridin-2-aldehyde and derived Schiff base ligands [153].

In particular, conductivity measurements and NMR measurements on solutions of $[Rh(diolefin)(CH_2(pz)_2)]ClO_4$ complexes points [116] to the presence of an association process involving the following equilibrium:

$$2[Rh(TFB)(CH_2(pz)_2)]ClO_4 \rightleftharpoons [Rh_2(TFB)_2(CH_2(pz)_2)_2][ClO_4]_2 \quad (46)$$

The X-ray structure of the $[Rh(COD)(CH_2(pz)_2)]ClO_4$ complex shows a distorted square–planar coordination in a mononuclear arrangement [116].

Mixed diolefin rhodium complexes of formula $[Rh(TFB)(diolefin)]ClO_4$ can be prepared by reacting $[Rh(\mu\text{-}Cl)(TFB)]_2$ with $AgClO_4$ in the presence of the appropriate diolefin (1,5-cyclooctadiene, 2-methyl-1,3-butadiene or 2,3-dimethyl-1,3-butadiene) [152].

A general route for the preparation of mixed ligand cationic complex of formula $[Rh(TFB)LL']ClO_4$ is the treatment of neutral RhCl(TFB)L complexes with silver salts and L′ (Scheme 28). Thus, RhCl(TFB)(PhN=CPhNHPh) reacts with $AgClO_4$ and PPh_3 to yield $[Rh(TFB)(PhN{=}CPhNHPh)PPh_3]ClO_4$ [123].

Cationic trimethyltetrafluorobenzobarrene complexes of the type $[Rh(Me_3TFB)L_2]PF_6$ (L = O, N, P, As, Sb-donor ligands) have been prepared by reaction of $[Rh(\mu\text{-}Cl)(Me_3TFB)]_2$ with $AgPF_6$ and subsequent addition of dimethylsulfoxide, pyridine, acetonitrile, triphenylphosphine, triphenylarsine, or triphenylstibiine [154]. The addition of a stoichiometric amount of triphenylphosphine to $[Rh(Me_3TFB)(Me_2CO)_x]PF_6$ leads to the formation of $[Rh(Me_3TFB)(PPh_3)(Me_2CO)]PF_6$, that reacts with donor ligands such as dimethylsulfoxide to yield $[Rh(Me_3TFB)(PPh_3)(Me_2SO)]PF_6$ [154].

A family of ion-pair complexes of formula $[M(Me_xTFB)(tpzm)][MCl_2(Me_xTFB)]$ (M = Rh, Ir; $x = 3, 0$) was obtained by reacting $[M(\mu\text{-}Cl)(Me_xTFB)]_2$ with tris(pyrazol-1-yl)methane in a 1:1 molar ratio [10]. The related $[Rh(TFB)(Hbpt)][RhCl_2(TFB)]$ (Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole) compound was similarly prepared [112].

3.3.2. Di- and polynuclear complexes

Dinuclear $[Rh_2(TFB)_2(\mu\text{-}R\text{-}napy)_2][ClO_4]_2$ complexes are isolated upon addition of stoichiometric amounts of R-napy (R = R = H or 2-Me), whilst mononuclear cationic complexes of formula $[Rh(TFB)(napy)_2]ClO_4$, or $[Rh(Me_3TFB)(napy)_2]ClO_4$, are obtained from an excess of the 1,8-naphthyridine (napy) ligand with $[Rh(TFB)(Me_2CO)_x]ClO_4$ species. It is interesting to point out that, under similar conditions, the tetrafluorobenzobarrele diolefin promotes the formation of dinuclear species, $[Rh_2(TFB)_2(\mu\text{-}2\text{-}Me\text{-}napy)_2][ClO_4]_2$, whilst 1,5-cyclooctadiene favours the exclusive formation of the mononuclear $[Rh(COD)(2\text{-}Menapy)_2]ClO_4$ complex (Eq. (47)) [105]:

$$y[\mathrm{Rh(diolefin)(Me_2CO)_x}]\mathrm{ClO_4} + y\,2\text{-Me-napy} \rightarrow [\mathrm{Rh_y(diolefin)_y(2\text{-}Me\text{-}napy)_y}][\mathrm{ClO_4}]_y + yx\,\mathrm{Me_2CO} \quad (47)$$

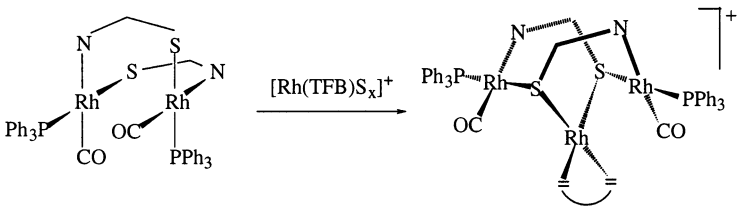
diolefin = TFB, $y = 2$; diolefin = COD, $y = 1$.

The dinuclear $[(\mathrm{TFB})\mathrm{Rh}(\mu\text{-dipy})\mathrm{Rh(CO)(PPh_3)_2}]\mathrm{ClO_4}$ complex was prepared by reacting Rh(dipy)(TFB) (dipy = 2-2′dipyridilamine) with $[\mathrm{Rh(CO)(PPh_3)_2(Me_2CO)_2}]\mathrm{ClO_4}$ [109]. $[\{\mathrm{Rh(TFB)}\}_2(\mu\text{-L})]\mathrm{BF_4}$ was isolated by adding the 3,5-bis(4-methylpyrazol-1-yl)-4-methylpyrazole ligand to $[\mathrm{Rh}(\mu\text{-Cl})(\mathrm{TFB})]_2$ in the presence of KOH and $\mathrm{NaBF_4}$ [10]. The related dinuclear complex $[\{\mathrm{Rh(TFB)}\}_2(\mu\text{-bpt})]\mathrm{ClO_4}$ was prepared by treating $[\mathrm{Rh(TFB)(Hbpt)}]\mathrm{ClO_4}$ species with $[\mathrm{Rh}(\mu\text{-OMe})(\mathrm{TFB})]_2$. A cationic dinuclear $[\mathrm{Rh_2(TFB)_2(L)_2}][\mathrm{ClO_4}]_2$ complex was obtained by reaction of $[\mathrm{Rh(TFB)(Me_2CO)_x}]\mathrm{ClO_4}$ with 1,6-bis(2′-benzimidazolyl)-2,5-dithiahexane [115]. Similarly, cationic complexes of formula $[\mathrm{Rh}_n(\mathrm{TFB})_n(\mathrm{L})_n][\mathrm{ClO_4}]_n$ were prepared by reaction of $[\mathrm{Rh(TFB)(Me_2CO)_x}]\mathrm{ClO_4}$ with pyrazine, 4,4′-bipyridine [102], pyridazine or 4,6-dimethyl-pyridimine [103].

Cationic heterovalent $[\mathrm{C_5Me_5})\mathrm{LRh(Pz)_2Rh(TFB)}]\mathrm{ClO_4}$ (L = MeCN or Hpz) complexes can be prepared by treating the neutral dinuclear $(\mathrm{C_5Me_5})\mathrm{ClRh(Pz)_2Rh(TFB)}$ compound with $\mathrm{AgClO_4}$ in the presence of the appropriate ligand [137].

The syntheses of homo- and hetero-trinuclear complexes of the type $[\mathrm{Rh_2M}(\mu_3\text{-}\mathrm{OMe}_x\mathrm{napy})(\mathrm{TFB})_2(\mathrm{CO})_2]\mathrm{ClO_4}$ (M = Rh, Ir; $\mathrm{OMe}_x\mathrm{napy}$ = 1,8-napththyridine-2-one and 5,7-dimethyl-1,8-napththyridine-2-one) can be performed by reacting $[\mathrm{Rh_2}(\mu\text{-}\mathrm{OMe}_x\mathrm{napy})(\mathrm{TFB})]_n$ complexes [113,155] that still possess at least one uncoordinated donor atom, with $[\mathrm{M(CO)_2(Me_2CO)_x}]\mathrm{ClO_4}$ species [113,155]. The formation of these type of cationic complexes can be achieved if a sterically undemanding fragment, such as $\mathrm{M(CO)_2}^+$, occupies the central position in the linear trinuclear complexes, in such way that migration of ligands between the metal fragments frequently occurs to achieve this special arrangement [113,155]. Chemical oxidation processes of these trinuclear complexes have been observed [155,156].

Trinuclear angular aggregates of rhodium of general formula $[\mathrm{Rh_3}(\mu_3\text{-}\mathrm{L})_2(\mathrm{TFB})_2(\mathrm{L}')_2]\mathrm{ClO_4}$, can be prepared by reaction of the dinuclear complexes $[\mathrm{Rh}(\mu\text{-}\mathrm{SC_5H_4N})(\mathrm{TFB})]_2$ and $[\mathrm{Rh}(\mu\text{-}\mathrm{C_7H_4NS_2})(\mathrm{TFB})]_2$ with cationic species, $[\mathrm{Rh(L')_2(Me_2CO)_x}]\mathrm{ClO_4}$ ($\mathrm{L'_2}$ = TFB, $(\mathrm{CO})_2$, $(\mathrm{CO})\mathrm{PPh_3}$). The X-ray structure of the $[\mathrm{Rh_3}(\mu_3\text{-}\mathrm{C_7H_4NS_2})_2(\mathrm{CO})_2(\mathrm{PPh_3})_2(\mathrm{TFB})]\mathrm{ClO_4}$ complex, prepared by reacting $[\mathrm{Rh}(\mu\text{-}\mathrm{C_7H_4NS_2})(\mathrm{CO})\mathrm{PPh_3}]_2$ with $[\mathrm{Rh(TFB)(Me_2CO)_x}]\mathrm{ClO_4}$ (Eq. 48), shows two benzothiazole-2-thiolate ligands, acting as triple bridges through the nitrogen and one sulfur atom, interacting with all three rhodium atoms [157]:



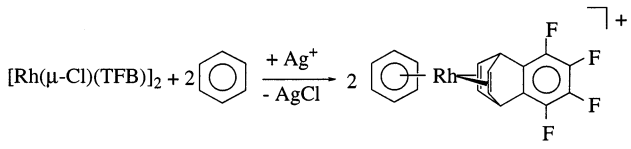
(48)

Similarly the addition of $[Rh(TFB)(Me_2CO)_x]ClO_4$ to the double bridged dinuclear dirhodium complex $[Rh(\mu\text{-}SPh)(TFB)]_2$, yields $[Rh_3(\mu_3\text{-}SPh)_2(TFB)_3]ClO_4$. The crystal structure of the analogous $[Rh_3(\mu_3\text{-}SPh)_2(COD)_3]ClO_4$ complex shows a triangular arrangement of rhodium atoms capped on each side by triple bridging phenylthio groups [131].

Cationic tetranuclear mixed-valence complexes of rhodium(III) and rhodium(I) or iridium(I) of formula $[\{(C_5Me_5)LRh(bim)M(TFB)\}_2]ClO_4$ (M = Rh, Ir) were prepared by reacting $[Rh(C_5Me_5)(Hbim)L]ClO_4$ (L = NC′Bu, $P(OEt)_3$, PPh_3) [136] with M(acac)(TFB). An X-ray diffraction study on the analogous $[\{(C_5Me_5)(P(OEt)_3)Rh(bim)Rh(COD)\}_2]ClO_4$ complex confirms the proposed tetranuclear formulation with two biimidazolate ligands bridging the rhodium atoms in an unsymmetrical tetradentate manner [142].

3.3.3. Mono- and dinuclear arene complexes

Cationic complexes of the type $[Rh(TFB)(\eta^6\text{-arene})]^+$ (arene = C_6H_6, C_6H_5OH, C_6H_5Me, C_6H_5OMe, 1,3-$C_6H_4(OMe)_2$, 1,4-$C_6H_4Me_2$, 1,3,5-$C_6H_3Me_3$, 1,2,4,5-$C_6H_2Me_4$, C_6Me_6) [152,158] or $[Rh(Me_xTFB)(\eta^6\text{-arene})]^+$ (arene = C_6H_6, C_6H_5Me, 1,3-$C_6H_4Me_2$, 1,4-$C_6H_4Me_2$, 1,3,5-$C_6H_3Me_3$, 1,2,4,5-$C_6H_2Me_4$, C_6Me_6, C_6H_5Cl, C_6F_6, $C_{10}H_8$) [154,158,159] have been prepared by reacting $[Rh(\mu\text{-}Cl)(TFB)]_2$ with $AgClO_4$ or $AgPF_6$ and arenes, as illustrated in Eq. 49 for $[Rh(TFB)(\eta^6\text{-}C_6H_6)]^+$:



(49)

NMR studies in deuteroacetone on arene rhodium complexes show the existence of the following equilibrium (Eq. (50)):

$$[Rh(Me_xTFB)(\eta^6\text{-arene})]^+ + x\,Me_2CO \leftrightharpoons [Rh(Me_xTFB)(Me_2CO)_x]^+ + \text{arene} \quad (50)$$

The equilibrium displacement is directly related to the number of methyl groups, present in the arene, and it is displaced towards the right with decreasing methyl substitution on the arene ring. If the coordinated arene has a reduced donor capacity, as in the case of naphthalene, complete dissociation is observed [152,154,159]. The dissociation of the coordinated arene is less for the trimethyltetrafluorobenzobarrelene rhodium complexes than for the analogous tetrafluorobenzobarrelene rhodium derivatives. Thus, the trimethyltetrafluorobenzobarrelene rhodium complexes with 1,2,4,5-tetramethylbenzene hexamethylbenzene or 1,2,4,5-tetramethylbenzene show no dissociation in deuteroacetone. Furthermore, the $[Rh(Me_3TFB)(\eta^6\text{-}C_6Me_6)]ClO_4$ complex does not undergo any change upon dissolution in dimethylsulfoxide, whilst the analogous $[Rh(TFB)(\eta^6\text{-}C_6Me_6)]ClO_4$ reacts with dimethylsulfoxide to yield $[Rh(TFB)(DMSO)_2]ClO_4$ [152,159]. NMR systematic studies on analogous $[M(diolefin)(\eta^6\text{-arene})]ClO_4$ complexes indicate that the lability of the arene–metal bond is modified by the metal and the auxiliary diolefin in the order $Me_3TFB < TFB < COD$

[18,159]. The related complex $Rh(Me_3TFB)PhBPh_3$ presents a coordinated phenyl ring; NMR studies suggest that this arene group is not easily displaceable in non polar solvents [159].

Studies on the crystal structures of $[Rh(Me_xTFB)(\eta^6\text{-arene})]ClO_4$ complexes have revealed a systematic departure from planarity and relative disposition of the coordinated arene ring, adopting conformations between skew and boat. The observed conformations and the relative disposition of the arene ring with respect to the barrelene ligands, seems to be a compromise between the tendency to square–planar coordination of rhodium, the variations in the Rh–C(olefin) distances, and the effects of substitution in the arene and the corresponding electron distribution on it [152,158–160]. The crystal structures of related iridium complexes of formula $[Ir(Me_xTFB)(\eta^6\text{-arene})]ClO_4$ show that the electronic considerations proposed for rhodium complexes are also operative for the 18-electron iridium congeners. Their Ir–C(arene) distances show similar features and generally similar parameters to those for the corresponding rhodium analogues. It is of interest to point that although the distances of the olefinic carbons to the best least square-plane through the arene ring are similar in the cationic rhodium and iridium complexes, the iridium atom is slightly closer to the arene ring than is the rhodium atom in the corresponding complex [16,18,161].

Tetrafluorobarrelene rhodium arene complexes of indole (HIn) and N–indolyl gold(I) derivatives, $[Rh(Me_xTFB)(\eta^6\text{-HIn})]^+$ and $[Rh(Me_xTFB)(\mu\text{-In})AuPR_3]^+$, have been prepared by reacting $[Rh(\mu\text{-Cl})(Me_xTFB)]_2$ with HIn or $Au(In)PR_3$, in the presence of silver salts. In both complexes the ligand seems to be bonded to the rhodium atom via its six-membered ring [162,163]. The structure of $[Rh(Me_3TFB)(\eta^6\text{-HIn})]ClO_4$ has been established by X-ray diffraction showing the rhodium atom η^6-bonded to the puckered six-membered ring of the indole ligand [163].

Polycylic arene ligands also react with $[Rh(Me_xTFB)(Me_2CO)_x]^+$ species to yield $[Rh(Me_xTFB)(\eta^6\text{-arene}')]^+$ complexes (arene′ = $C_{10}H_8$, Ph_2, Ph_2CH_2, Ph_2CO) containing a coordinated phenyl ring [154,164,165]. Interestingly, the uncoordinated ring of the diphenylmethane complex allows further coordination. Thus, $[Rh(Me_3TFB)(\eta^6\text{-}Ph_2CH_2)]ClO_4$ react with $[Rh(Me_3TFB)(Me_2CO)_x]ClO_4$ or $Cr(CO)_3(\eta^6\text{-}Me_3B_3N_3Me_3)$ to yield the homo- or hetero-dinuclear complexes $[Rh(Me_3TFB)(Ph_2CH_2)Rh(Me_3TFB)]ClO_4$ and $[Rh(Me_3TFB)(Ph_2CH_2)Cr(CO)_3]ClO_4$ [164]. The formation of the latter complex is favoured by the high reactivity of the borazine–chromium bond [166]. Mononuclear hexamenthylborazine complexes of formula $[Rh(Me_3TFB)(\eta^6\text{-}Me_3B_3N_3Me_3)]PF_6$ have been prepared from the reaction between $[Rh(\mu\text{-Cl})(Me_3TFB)]_2$, $Me_3B_3N_3Me_3$ and $AgPF_6$ [167].

The coordination ability, towards barrelene rhodium moieties, of the non-benzenoid aromatic compound azulene has been also studied. Thus, $[Rh(Me_xTFB)(azulene)]^+$ complexes have been prepared by reacting $Rh(\mu\text{-Cl})(Me_xTFB)]_2$ with azulene in the presence of silver salts. The crystal structure of $[Rh(TFB)(azulene)]PF_6$ shows the rhodium atom bonded through the azulene five-membered ring. The bonding within the azulene ligand differs from that observed for the parent hydrocarbon. Furthermore, the five- and seven-membered rings of the ligand show some deviations from planarity [168].

3.4. Catalytic activity

Several mononuclear rhodium and dinuclear rhodium–tetrafluorobenzobarrelene complexes are shown to have catalytic properties. The catalytic studies have been concentrated in reduction reactions by molecular hydrogen or by hydrogen transfer from 2-propanol.

A systematic study on the hydrogenation reduction of olefins, several diolefins and 1-hexyne by $[Rh(TFB)(PPh_2Et)_2]ClO_4$ and $[Rh(TFB)\{P(p\text{-}RC_6H_4)_3\}_2]ClO_4$ complexes has been reported [150]. Since the substituent R (R = MeO, Me. F or Cl) in the $p\text{-}RC_6H_4$ group causes a progressive decrease in the basicity of the phosphine without steric effects it has been possible to examine the influence of this factor on the catalytic activity. The observed hydrogenation rates in dichloromethane are higher than those in oxygen donor solvents. The rate of hydrogenation of 1-heptene, isoprene and 1,3-cyclohexadiene follow a direct relation between basicity of the phosphine and the reduction rate. In contrast, when 1,4-cyclohexadiene was hydrogenated a reverse relation between reduction rate and basicity was observed, along with a high selectivity to the formation of cyclohexene. Interestingly 1-hexyne is hydrogenated to 1-hexene with very high selectivity [150].

Cationic rhodium complexes with Schiff-base ligands of formula $[Rh(TFB)(PyCH{=}NR)]ClO_4$, prepared by reaction of coordinated pyridin-2-aldehyde with primary amines, are active catalysts for the transfer of hydrogen from 2-propanol to acetophenone, in basic media. The rate of formation of 1-phenylethanol increases with the basicity of the parent amine [153]. Most probably, the more basic ligand favours the hydrogen abstraction from the coordinated isopropoxide to form the key $H\text{-}Rh\text{–}OCMe_2$ species.

Dinuclear dirhodium(I) complexes with bridging phenyl(2-pyridyl)amido ligands are also active catalyst precursors, in the presence of potassium hydroxide, for the transfer of hydrogen in refluxing 2-propanol to cyclohexene and acetophenone [124]. Finally, the heterobinuclear complex $(PPh_3)_2(CO)HRu(\mu\text{-}Cl)(\mu\text{-}pz)Rh(TFB)$, as well as the previously mentioned iridium analogue, also catalyses the hydrogen transfer from 2-propanol to cyclohexanone [22].

4. Concluding remarks

The fluorinated barrelene diolefins, and especially the tetrafluorobenzobarrelene (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene) diolefin, have remarkable potential in coordination chemistry. Their chemical behaviour towards iridium and rhodium shows some special characteristics due to the influence of the rather electron-withdrawing character of the tetrafluorobarrelene group and, particularly, the smaller bite angle of the tetrafluorobenzobarrelene diolefin. The synthesis of these tetrafluorobenzobarrelene compounds has promoted the development of a rich chemistry, including catalysis, of neutral and cationic complexes containing the iridium or rhodium–tetrafluorobenzobarrelene moieties, which show significant differences with respect to the chemistry of the typical metal-1,5-cyclooctadiene

moieties. These differences are particularly marked for iridium that especially favours the isolation of five-coordinated complexes, as the interesting starting material $IrCl(TFB)_2$. We believe that there is a door open to explore new chemistry based on metal–tetrafluorobezobarrelene moieties.

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References

[1] G. Giordano, R.H. Crabtree, Inorg. Synth. 19 (1979) 218.
[2] J.L. Herde, J.C. Lambert, C.V. Senoff, Inorg. Synth. 15 (1974) 18.
[3] E.W. Abel, M.A. Bennet, G. Wilkinson, J. Chem. Soc. (1959) 3178.
[4] R. Usón, L.A. Oro, J.A. Cabeza, Inorg. Synth. 23 (1985) 126.
[5] R.S. Dickson, Organometallic Chemistry of Rhodium and Iridium, Academic Press, London, 1983.
[6] (a) P.R. Sharp, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon Press, Oxford, 1995, Ch. 5.2. (b) R.P. Hughes, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 5, Pergamon Press, Oxford, 1982, Ch. 35.
[7] (a) J.D. Atwood, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon Press, Oxford, 1995, Ch. 5.3. (b) G.J. Leigh, R.L. Richards, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 5, Pergamon Press, Oxford, 1982, Ch. 36.
[8] A.J. Tomlinson, A.G. Massey, J. Organomet. Chem. 8 (1967) 321.
[9] D.M. Roe, A.G. Massey, J. Organomet. Chem. 28 (1971) 273.
[10] R.M. Claramunt, C. Lopez, D. Sanz, J. Elguero, D. Carmona, M. Esteban, L.A. Oro, M. Begtrup, J. Organomet. Chem. 412 (1991) 259.
[11] (a) M.A. Esteruelas, M.P. García, A.M. López, L.A. Oro, N. Ruiz, C. Schlünken, C. Valero, H. Werner, Inorg. Chem. 31 (1992) 5580. (b) A.J. Edwards, M.A. Esteruelas, F.J. Lahoz, A.M. López, E. Oñate, L.A. Oro, J.I. Tolosa, Organometallics 16 (1997) 1316. (c) A. Castillo, M.A. Esteruelas, E. Oñate, N. Ruiz, J. Am. Chem. Soc. 119 (1997) 9691.
[12] M. Valderrama, M. Scotti, A. Rojas, Polyhedron 4 (1985) 1585.
[13] D.R. Baghurst, D.M.P. Mingos, M.J. Watson, J. Organomet. Chem. 368 (1989) C43.
[14] (a) D.R. Anton, R.H. Crabtree, Organometallics 2 (1983) 621. (b) R.H. Crabtree, R.J. Uriarte, Inorg. Chem. 22 (1983) 4152.
[15] (a) A.R. Fraser, P.H. Bird, S.A. Bezman, J.R. Shapley, R. White, J.A. Osborn, J. Am. Chem. Soc. 95 (1973) 597. (b) S.A. Bezman, P.H. Bird, A.R. Fraser, J.A. Osborn, Inorg. Chem. 19 (1980) 3755.
[16] R. Usón, L.A. Oro, D. Carmona, M.A. Esteruelas, C. Foces-Foces, F.H. Cano, S. García-Blanco, J. Organomet. Chem. 254 (1983) 249.
[17] A.L. Onderdelinden, A. van der Ent, Inorg. Chim. Acta 6 (1972) 420.

[18] R. Usón, L.A. Oro, D. Carmona, M.A. Esteruelas, C. Foces-Foces, F.H. Cano, S. García-Blanco, A. Vázquez de Miguel, J. Organomet. Chem. 273 (1984) 111.
[19] R. Usón, L.A. Oro, D. Carmona, M.A. Esteruelas, J. Organomet. Chem. 263 (1984) 109.
[20] W. Chen, A.J. Edwards, M.A. Esteruelas, F.J. Lahoz, M. Oliván, L.A. Oro, Organometallics 15 (1996) 2185.
[21] W. Chen, M.A. Esteruelas, M. Martín, M. Oliván, L.A. Oro, J. Organomet. Chem. 534 (1997) 95.
[22] M.P. García, A.M. López, M.A. Esteruelas, F.J. Lahoz, L.A. Oro, J. Organomet. Chem. 388 (1990) 365.
[23] (a) L.H. Sommer, J.E. Lyons, H.J. Fujimoto, J. Am. Chem. Soc. 91 (1969) 705. (b) F.J. Harrod, C.A. Smith, K.A. Thank, J. Am. Chem. Soc. 94 (1972) 8321. (c) J.P. Fawcett, J.F. Harrod, J. Organomet. Chem. 113 (1976) 245. (d) M.A. Bennett, R. Charles, P. Fraser, Aust. J. Chem. 30 (1977) 1201. (e) C.E. Johnson, B.J. Fisher, R. Eisenberg, J. Am. Chem. Soc. 105 (1983) 7772. (f) C.E. Johnson, R. Eisenberg, J. Am. Chem. Soc. 107 (1985) 3148. (g) C.E. Johnson, R. Eisenberg, J. Am. Chem. Soc. 107 (1985) 6531.
[24] M.A. Esteruelas, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, R.M. Claramunt, C. López, J. Elguero, M. Begtrup, J. Organomet. Chem. 344 (1988) 93.
[25] (a) J.F. Young, R.D. Gillard, G. Wilkinson, J. Chem. Soc. (1964) 5176. (b) K. Vrieze, H.C. Volger, A.P. Praat, J. Organomet. Chem. 14 (1968) 185. (c) G. Mestroni, A. Camus, G. Zassinovich, J. Organomet. Chem. 73 (1974) 119. (d) R. Usón, L.A. Oro, M.J. Fernández, M.T. Pinillos, Inorg. Chim. Acta 39 (1980) 57.
[26] (a) R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 93 (1971) 3089. (b) C. Claver, J.C. Rodríguez, A. Ruiz, J. Organomet. Chem. 251 (1983) 369.
[27] (a) M.A. Esteruelas, F.J. Lahoz, M. Oliván, E. Oñate, L.A. Oro, Organometallics 13 (1994) 3315. (b) M.A. Esteruelas, L.A. Oro, J. Schrickel, Organometallics 16 (1997) 796.
[28] M.J. Fernández, M.A. Esteruelas, M. Covarrubias, L.A. Oro, J. Organomet. Chem. 316 (1986) 343.
[29] M.A. Esteruelas, F.J. Lahoz, M. Oliván, E. Oñate, L.A. Oro, Organometallics 14 (1995) 3486.
[30] (a) W.M. Rees, M.R. Churchill, J.C. Fettinger, J.D. Atwood, Organometallics 4 (1985) 2179. (b) W.M. Rees, J.D. Atwood, Organometallics 4 (1985) 402. (c) M.R. Churchill, J.C. Fettinger, W.M. Rees, J.D. Atwood, J. Organomet. Chem. 308 (1986) 361. (d) H.E. Bryndza, W. Tam, Chem. Rev. 88 (1988) 1163.
[31] S.L. Randall, C.A. Miller, R.F. See, M.R. Churchill, T.S. Janick, C.H. Lake, J.D. Atwood, Organometallics 13 (1994) 5088.
[32] (a) L.H. Chan, E.G. Rochow, J. Organomet. Chem. 9 (1967) 231. (b) K. Farmey; M. Kilner, C. Midcalf, J. Chem. Soc. (1970) 2279. (c) K. Kilner, Adv. Organomet. Chem. 10 (1972) 115.
[33] M.A. Esteruelas, O. Nürnberg, M. Oliván, L.A. Oro, H. Werner, Organometallics 12 (1993) 3264.
[34] M.A. Esteruelas, F.J. Lahoz, M. Oliván, E. Oñate, L.A. Oro, Organometallics 13 (1994) 4246.
[35] (a) M.J. Fernández, M. Esteruelas, M.S. Jiménez, L.A. Oro, Organometallics 5 (1986) 1519. (b) M.J. Fernández, M.A. Esteruelas, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, Organometallics 6 (1987) 1751.
[36] M.J. Fernández, M.A. Esteruelas, M. Covarrubias, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, Organometallics 8 (1989) 1158.
[37] M.J. Fernández, M.A. Esteruelas, L.A. Oro, J. Ruiz, A.J. Smith, P.M. Maitlis, J. Organomet. Chem. 330 (1987) 179.
[38] M.A. Esteruelas, M. Oliván, L.A. Oro, Organometallics 15 (1996) 814.
[39] (a) J. Halpern, Acc. Chem. Res. 15 (1982) 332. (b) D. Milstein, Acc. Chem Res. 17 (1984) 221. (c) B.P. Cleary, R. Mehta, R. Eisenberg, Organometallics 14 (1995) 2297.
[40] (a) K.C. Brinkman, A.J. Blakeney, W. Krone-Schmidt, J. Gladysz, Organometallics 3 (1984) 1326. (b) U. Schubert, J. Müller J. Organomet. Chem. 373 (1989) 165. (c) D.L. Thorn, R.L. Harlow, Inorg. Chem. 29 (1990) 2017. (d) P. Hofmann, H. Heiss, P. Neiteler, G. Müller, J. Hachmann, Angew. Chem Int. Ed. Engl. 29 (1990) 880. (e) B.J. Rappoli, J.M. McFarland, J.S. Thompson, J.D. Atwood, J. Coord. Chem. 21 (1990) 147. (f) W. Lin, S.R. Wilson, G.S. Girolami, J. Am. Chem. Soc. 15 (1993) 3022.
[41] M. Aizenberg, D. Milstein, Angew. Chem. Int. Ed. Engl. 33 (1994) 317.

[42] (a) J.J. Eisch, A.M. Piotrowski, S.K. Brownstein, E.J. Gabe, F.L. Lee, J. Am. Chem. Soc. 107 (1985) 7219. (b) S.K. Brownstein, E.J. Gabe, N. Fong Han, F.L. Lee, Y. Le Page, A.M. Piotrowski, J.J. Eisch, J. Chem. Res (S) (1994) 214.
[43] H. Yamashita, M. Tanaka, M. Goto, Organometallics 12 (1993) 988.
[44] T. Takao, H. Suzuki, M. Tanaka, Organometallics 13 (1994) 2554.
[45] J. Yin, J. Klosin, K.A. Abboud, W.M. Jones, J. Am. Chem. Soc. 117 (1995) 3298.
[46] M.A. Esteruelas, F.J. Lahoz, A.M. López, E. Oñate, L.A. Oro, Organometallics 13 (1994) 1669.
[47] F.G. Glocking, J.G. Irwin, Inorg. Chim. Acta 6 (1972) 355.
[48] M. Kretschmer, P.S. Pregosin, A. Albinati, A. Togni, J. Organomet. Chem. 281 (1985) 365.
[49] G.R. Clark, B.W. Skelton, T.N. Waters, Inorg. Chim. Acta 281 (1985) 365.
[50] H. Lehner, D. Matt, P.S. Pregosin, L.M. Venanzi, A. Albinati, J. Am. Chem. Soc. 104 (1982) 6825.
[51] P. Bird, J.F. Harrod, K.A. Than, J. Am. Chem. Soc. 96 (1974) 1222.
[52] R.A. Sánchez-Delgado, V. Herrera, C. Bianchini, D. Masi, C. Mealli, Inorg. Chem. 32 (1993) 3766.
[53] M.R. Churchill, K.-K.G. Lin, J. Am. Chem. Soc. 96 (1974) 76.
[54] (a) M.J. Auburn, S.L. Grundy, S.R. Stobart, M.J. Zaworotko, J. Am. Chem. Soc. 107 (1985) 266. (b) M. Aizenberg, D. Milstein, Organometallics 15 (1996) 3317.
[55] (a) Y.K. Ho, J.J. Zuckerman, J. Organomet. Chem. 49 (1973) 1. (b) T.D. Tilley, in: S. Patai, Z. Rappoport, (Eds.), The chemistry of Organic Silicon Compounds, Wiley, New York, 1989.
[56] E. Meléndez, A.M. Arif, M.L. Ziegler, R.D. Ernest, Angew. Chem. Int. Ed. Engl. 27 (1988) 1099.
[57] M.R. Churchill, K.K. Lin, Inorg. Chem. 14 (1975) 1675.
[58] (a) D. Bright, O.S. Mills, J. Chem. Soc. Chem. Commun. (1967) 245. (b) A.J. Carty, D.P. Madden, M. Mathew, G.J. Palenik, T. Birchall, J. Chem. Soc. Chem. Commun. (1970) 1664. (c) V.G. Andrinov, Yu.T. Struchkov, Koord. Khim. 4 (1978) 937. (d) A. Klose, E. Salari, R. Ferguson, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics 12 (1993) 2414.
[59] T. Carofiglio, S. Stella, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Chem. Soc. Dalton Trans. (1989) 1957.
[60] M.P. García, M.A. Esteruelas, M. Martín, L.A. Oro, J. Organomet. Chem. 467 (1994) 151.
[61] M.P. García, A.M. López, M.A. Esteruelas, F.J. Lahoz, L.A. Oro, J. Chem. Soc. Dalton Trans. (1990) 3465.
[62] L.A. Oro, D. Carmona, M.A. Esteruelas, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 307 (1986) 83.
[63] L.A. Oro, D. Carmona, M.A. Esteruelas, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 258 (1983) 357.
[64] J. Peone Jr., L. Vaska, Angew. Chem. Int. Ed. Engl. 10 (1971) 511.
[65] R. Usón, L.A. Oro, D. Carmona, M.A. Esteruelas, Inorg. Chim. Acta 73 (1983) 275.
[66] P.A. Chaloner, M.A. Esteruelas, F. Joó, L.A. Oro, Homogeneous Hydrogenation; Kluwer Academic Publishers, Dordrecht, 1994, Ch. 2, Sec. 2.2.2.
[67] M.A. Esteruelas, M.P. García, A.M. López, L.A. Oro, Organometallics 10 (1991) 127.
[68] M.A. Esteruelas, A.M. López, L.A. Oro, A. Pérez, M. Schulz, H. Werner, Organometallics 12 (1993) 1823.
[69] R.H. Crabtree, G. Morris, J. Organomet. Chem. 135 (1977) 395.
[70] W. Chen, M.A. Esteruelas, J. Herrero, F.J. Lahoz, M. Martín, E. Oñate, L.A. Oro, Organometallics 16 (1997) 6010.
[71] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[72] F.H. Allen, O. Kennard, 3D Search and Research using the Cambridge Structure Database Chem. Des. Automation News. 8 1 (1993) 31–37.
[73] R.H. Crabtree, H. Felkin, T. Fillebeen-Khan, G.E. Morris, J. Organomet. Chem. 168 (1979) 183.
[74] M.I. Bruce, Chem. Rev. 91 (1991) 197.
[75] (a) R. Usón, L.A. Oro, R. Sariego, M.A. Esteruelas, J. Organomet. Chem. 214 (1981) 399. (b) M.A. Esteruelas, M. Oliván, L.A. Oro, M. Schulz, E. Sola, H. Werner, Organometallics 11 (1992) 3659.

[76] P.A. Chaloner, M.A. Esteruelas, F. Joó, L.A. Oro, Homogeneous Hydrogenation, Kluwer Academic Publishers, Dordrecht, 1994; Ch. 3, Sec. 3.3.3.
[77] (a) M.A. Esteruelas, E. Sola, L.A. Oro, H. Werner, U. Meyer, J. Mol. Catal. 45 (1988) 1. (b) M.A. Esteruelas, C. Valero, L.A. Oro, U. Meyer, H. Werner, Inorg. Chem. 30 (1991) 1159. (c) M.A. Esteruelas, M.P. García, M. Martín, L.A. Oro, J. Mol. Catal. 87 (1994) 151. (d) R.A. Sánchez-Delgado, M. Rosales, M.A. Esteruelas, L.A. Oro, J. Mol. Catal. A. 96 (1995) 231. (e) M.A. Esteruelas, L.A. Oro, Chem. Rev. 98 (1998) 577.
[78] L.A. Oro, D. Carmona, J. Reyes, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Dalton Trans. (1986) 31.
[79] M.P. García, A. Portilla, L.A. Oro, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 322 (1987) 111.
[80] (a) R.H. Crabtree, Platinum Met. Rev. 22 (1978)126. (b) R.H. Crabtree, Acc. Chem. Res. 12 (1979) 331 (c) R. Usón, L.A. Oro, M.J. Fernández, J. Organomet. Chem. 193 (1980) 127.
[81] R.H. Crabtree, M.F. Mellea, J.M. Mihelcic, J.M. Quirk, J. Am. Chem. Soc. 104 (1982) 107.
[82] (a) R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 98 (1976) 2143. (b) M.A. Esteruelas, I. González, J. Herrero, L.A. Oro, J. Organomet. Chem. 551 (1998) 49.
[83] (a) J. Halpern, D.P. Riley, A.S.C. Chan, J.J. Pluth, J. Am. Chem. Soc. 99 (1977) 8055. (b) A.S.C. Chan, J.J. Pluth, J. Halpern, Inorg. Chim. Acta 37 (1979) L477. (c) A.S.C. Chan, J. Halpern, J. Am. Chem. Soc. 102 (1980) 838.
[84] R.H. Crabtree, J.M. Quirk, J. Organomet. Chem. 199 (1980) 99.
[85] K.A. Beveridge, G.W. Bushnell, K.R. Dixon, D.T. Eadie, S.R. Stobart, J. Am. Chem. Soc. 104 (1982) 920.
[86] L.A. Oro, M.J. Fernández, M.A. Esteruelas, M.J. Jiménez, J. Mol. Catal. 37 (1986) 151.
[87] A. Millán, M.J. Fernández, P. Bentz, P.M. Maitlis, J. Mol. Catal. 26 (1984) 89.
[88] M.A. Esteruelas, M. Oliván, L.A. Oro, J.I. Tolosa, J. Organomet. Chem. 487 (1995) 143.
[89] (a) I. Ojima, M. Kumagai, Y. Nagai, J. Organomet. Chem. 66 (1974) C14. (b) M.F. Lappert, R.R. Maskell, J. Organomet. Chem. 264 (1984) 217.
[90] H.M. Dickers, R.N. Haszeldine, A.P. Mather, R.V. Parish, J. Organomet. Chem. 161 (1978) 91.
[91] K.A. Brady, T.A. Nile, J. Organomet. Chem. 206 (1981) 299.
[92] I. Ojima, N. Clos, R.J. Donovan, P. Ingallina, Organometallics 9 (1990) 3127.
[93] M.A. Esteruelas, L.A. Oro, C. Valero, Organometallics 10 (1991) 462.
[94] M.A. Esteruelas, J. Herrero, L.A. Oro, Organometallics 12 (1993) 2377.
[95] C.H. Jun, R.H. Crabtree, J. Organomet. Chem. 447 (1993) 177.
[96] M.A. Esteruelas, A.M. López, L.A. Oro, J.I. Tolosa, J. Mol. Catal. A Chem. 96 (1995) 21.
[97] (a) H. Werner, U. Meyer, M.A. Esteruelas, E. Sola, L.A. Oro, J. Organomet. Chem. 366 (1989) 187. (b) C. Bohanna, M.A. Esteruelas, J. Herrero, A.M. López, L.A. Oro, J. Organomet. Chem. 498 (1995) 199.
[98] (a) A.M. Echavarren, J. López, A. Santos, A. Romero, J.A. Hermoso, A. Vegas, Organometallics 10 (1991) 2371. (b) A. Santos, J. López, J. Montoya, P. Noheda, A. Romero, A.M. Echavarren, Organometallics 13 (1994) 3605. (c) C. Bianchini, P. Frediani, D. Masi, M. Peruzzini, F. Zanobini, Organometallics 13 (1994) 4616.
[99] A.J. Chalk, F.G. Harrod, J. Am. Chem. Soc. 87 (1965) 16.
[100] J. Chatt, L.M. Venanzi, J. Chem. Soc. (1957) 4735.
[101] D.R. Baghurst, D.M.P. Mingos, J. Organomet. Chem. 384 (1990) C57.
[102] R. Usón, L.A. Oro, D. Carmona, M. Esteban, J. Organomet. Chem. 220 (1981) 103.
[103] R. Usón, L.A. Oro, D. Carmona, M. Esteban, R. Claramunt, J. Elguero, Polyhedron 3 (1984) 213.
[104] M.P. García, J.A. Manero, L.A. Oro, M.C. Apreda, F.H. Cano, C. Foces-Foces, J.G. Haasnoot, R. Prins, J. Reedijk, Inorg. Chim. Acta 122 (1986) 235.
[105] A. Tiripicchio, M. Tiripicchio Camellini, R. Usón, L.A. Oro, M.A. Ciriano, F. Viguri, J. Chem. Soc. Dalton Trans. (1984) 125.
[106] L.A. Oro, M.T. Pinillos, C. Tejel, J. Organomet. Chem. 280 (1985) 261.
[107] L.A. Oro, M.A. Ciriano, B.E. Villarroya, A. Tiripicchio, F.J. Lahoz, J. Chem. Soc. Chem. Commun. (1984) 521.

[108] L.A. Oro, M.A. Ciriano, B.E. Villarroya, A. Tiripicchio, F.J. Lahoz, J. Chem. Soc. Dalton Trans. (1985) 1891.
[109] L.A. Oro, M.A. Ciriano, F. Viguri, C. Foces-Foces, F.H. Cano, Inorg. Chim. Acta 115 (1986) 65.
[110] M. Valderrama, H. Rafart, L.A. Oro, Transit. Met. Chem. 6 (1981) 221.
[111] F. Bonati, L.A. Oro, M.T. Pinillos, Polyhedron 4 (1985) 357.
[112] M.P. García, M. Martin, L.A. Oro, Inorg. Chim. Acta 191 (1992) 221.
[113] M.A. Ciriano, B.E. Villarroya, L.A. Oro, Inorg. Chim. Acta 120 (1986) 43.
[114] R. Usón, L.A. Oro, M. Esteban, A.M. Cuadro, P. Navarro, J. Elguero, Transit. Met. Chem. 7 (1982) 234.
[115] L.A. Oro, D. Carmona, J. Reedijk, Inorg. Chim. Acta 71 (1983) 115.
[116] L.A. Oro, M. Esteban, R.M. Claramunt, J. Elguero, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 276 (1984) 79.
[117] A.P. Sadimenko, S.S. Basson, Coord. Chem. Rev. 147 (1996) 247.
[118] R. Usón, L.A. Oro, M.A. Ciriano, M.T. Pinillos, A. Tiripicchio, M. Tiripicchio-Camellini, J. Organomet. Chem. 205 (1981) 247.
[119] R. Usón, L.A. Oro, M.A. Ciriano, M.C. Bello, J. Organomet. Chem. 240 (1982) 199.
[120] L.A. Oro, M.T. Pinillos, C. Tejel, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Dalton Trans. (1986) 1087.
[121] L.A. Oro, M.T. Pinillos, C. Tejel, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Dalton Trans. (1988) 1927.
[122] A. Tiripicchio, M. Tiripicchio-Camellini, R. Usón, L.A. Oro, M.A. Ciriano, M.T. Pinillos, J. Organomet. Chem. 224 (1982) 207.
[123] F.J. Lahoz, A. Tiripicchio, M. Tiripicchio-Camellini, L.A. Oro, M.T. Pinillos, J. Chem. Soc. Dalton Trans. (1985) 1487.
[124] F.J. Lahoz, F. Viguri, M.A. Ciriano, L.A. Oro, C. Foces-Foces, F.H. Cano, Inorg. Chim. Acta 128 (1987) 119.
[125] M.A. Ciriano, B.E. Villarroya, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 366 (1989) 377.
[126] A.M. Manotti Lanfredi, A. Tiripicchio, R. Usón, L.A. Oro, M.A. Ciriano, B.V. Villarroya, Inorg. Chim. Acta 88 (1984) L9.
[127] L.A. Oro, M.A. Ciriano, F. Viguri, A. Tiripicchio, M. Tiripicchio-Camellini, F.J. Lahoz, New J. Chem. 10 (1986) 75.
[128] M.A. Ciriano, F. Viguri, J.J. Perez-Torrente, F.J. Lahoz, L.A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini, J. Chem. Soc. Dalton Trans. (1989) 25.
[129] M.T. Pinillos, M.P. Jarauta, L.A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini, J. Organomet. Chem. 339 (1988) 181.
[130] M.T. Pinillos, M.P. Jarauta, A. Elduque, F.J. Lahoz, L.A. Oro, J. Organomet. Chem. 514 (1996) 119.
[131] M.A. Ciriano, J.J. Pérez-Torrente, F.J. Lahoz, L.A. Oro, J. Chem. Soc. Dalton. Trans. (1992) 1831.
[132] L.A. Oro, M.T. Pinillos, M.P. Jarauta, Polyhedron 4 (1985) 325.
[133] M.A. Calvo, A.M. Manotti Lanfredi, L.A. Oro, M.T. Pinillos, C. Tejel, A. Tiripicchio, F. Ugozzoli, Inorg. Chem. 32 (1993) 1147.
[134] N.G. Connelly, A.C. Lyons, M.J. Fernandez, J. Modrego, L.A. Oro, J. Chem. Soc. Dalton. Trans. (1989) 683.
[135] M.J. Fernandez, J. Modrego, L.A. Oro, M.C. Apreda, F.H. Cano, C. Foces-Foces, Inorg. Chim. Acta 157 (1989) 61.
[136] L.A. Oro, D. Carmona, M. Esteban, Trends Organomet. Chem. 1 (1994) 565.
[137] L.A, Oro, D. Carmona, J. Reyes, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Dalton Trans. (1986) 31.
[138] L.A. Oro, D. Carmona, M.P. García, F.J. Lahoz, J. Reyes, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 296 (1985) C43.
[139] (a) M. Esteban, A. Pequerul, D. Carmona, F.J. Lahoz, A. Martín, L.A. Oro, J. Organomet. Chem. 404 (1991) 421. (b) M.A. Esteruelas, F.J. Lahoz, J.A. López, L.A. Oro, C. Schlünken, C. Valero, H. Werner, Organometallics 11 (1992) 2034.

[140] M. Scotti, M. Valderrama, S. Rojas, W. Kläui, J. Organomet. Chem. 301 (1986) 369.
[141] M.T. Pinillos, C. Tejel, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Dalton Trans. (1989) 1133.
[142] L.A. Oro, D. Carmona, M.P. Lamata, A. Tiripicchio, F.J. Lahoz, J. Chem. Soc. Dalton Trans. (1986) 15.
[143] J.J. Pérez-Torrente, M.A. Casado, M.A. Ciriano, F.J. Lahoz, L.A. Oro, Organometallics 35 (1996) 1782.
[144] C. Tejel, B.V. 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.
[145] R. Atencio, M.A. Casado, M.A. Ciriano, F.J. Lahoz, A. Tiripicchio, L.A. Oro, J. Organomet. Chem. 514 (1996) 103.
[146] C. Tejel, Y.M. Shi, M.A. Ciriano, A.J. Edwards, F.J. Lahoz, L.A. Oro, Angew. Chem. Int. Ed. Engl. 35 (1996) 633.
[147] C. Tejel, Y.M. Shi, M.A. Ciriano, A.J. Edwards, F.J. Lahoz, L.A. Oro, Angew. Chem. Int. Ed. Engl. 35 (1996) 1516.
[148] C. Tejel, Y.M. Shi, M.A. Ciriano, A.J. Edwards, F.J. Lahoz, J. Modrego, L.A. Oro, J. Am. Chem. Soc. 119 (1997) 6678.
[149] R. Usón, L.A. Oro, M. Valderrama, C. Claver, Synth. React. Inorg. Met.-Org. Chem. 9 (1979) 577.
[150] R. Usón, L.A. Oro, R. Sariego, M. Valderrama, C. Rebullida, J. Organomet. Chem. 197 (1980) 87.
[151] R. Usón, J. Gimeno, L.A. Oro, M. Valderrama, R Sariego, E. Martinez, Transit. Met. Chem. 6 (1981) 103.
[152] R. Usón, L.A. Oro, C. Foces-Foces, F.H. Cano, A. Vegas, M. Valderrama, J. Organomet. Chem. 215 (1981) 241.
[153] L.A. Oro, M.P. Lamata, M. Valderrama, Transit. Met. Chem. 8 (1983) 48.
[154] M. Valderrama, R. Ganz, R. Sariego, Transit. Met. Chem. 8 (1983) 160.
[155] B.E. Villarroya, L.A. Oro, F.J. Lahoz, A.J. Edwards, M.A. Ciriano, P.J. Alonso, A. Tiripicchio, M. Tiripicchio-Camellini, Inorg. Chim. Acta 250 (1996) 241.
[156] N.G. Connelly, A.C. Loyns, M.A. Ciriano, M.J. Fernandez, L.A. Oro, B.E. Villarroya, J. Chem. Soc. Dalton. Trans. (1989) 689.
[157] M.A. Ciriano, J.J. Perez-Torrente, F. Viguri, F.J. Lahoz, L.A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini, J. Chem. Soc. Dalton Trans. (1990) 1493.
[158] L.A. Oro, C. Foces-Foces, F.H. Cano, S. Garcia-Blanco, J. Organomet. Chem. 236 (1982) 385.
[159] R. Usón, L.A. Oro, C. Foces-Foces, F.H. Cano, S. Garcia-Blanco, M. Valderrama, J. Organomet. Chem. 229 (1982) 293.
[160] F.H. Cano, C. Foces-Foces, L.A. Oro, J. Organomet. Chem. 288 (1985) 225.
[161] F.H. Cano, C. Foces-Foces, J. Organomet. Chem. 291 (1985) 363.
[162] R. Usón, L.A. Oro, J.A. Cabeza, M. Valderrama, J. Organomet. Chem. 231 (1982) C81.
[163] R. Usón, L.A. Oro, J.A. Cabeza, C. Foces-Foces, F.H. Cano, S. Garcia-Blanco, J. Organomet. Chem. 246 (1983) 73.
[164] M. Valderrama, M. Scotti, P. Cifuentes, R. Ganz, Transit. Met. Chem. 9 (1984) 312.
[165] M. Valderrama, M. Scotti, E. Prati, J. Chem. Res. S (1985) 326.
[166] H. Werner, E. Deckelmann, Chimia 23 (1969) 195.
[167] M. Scotti, M. Valderrama, R. Ganz, H. Werner, J. Organomet. Chem. 286 (1985) 399.
[168] L.A. Oro, M. Valderrama, P. Cifuentes, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 276 (1984) 67.