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Preparation and reactivity of dinuclear complexes having the $M_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})$ core (M = Rh, Ir; Pz = pyrazolate)

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Abstract

The reaction of $[M_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(COD)_2]$ with carbon monoxide and bis(diphenylphosphino)methane yields the triply heterobridged complexes $[M_2(\mu\text{-Pz})(\mu\text{-SB}^t)(\mu\text{-dppm})(CO)_2]$, M = Rh, Pz = pz (**1**); M = Ir, Pz = pz (**2**), dmpz (**3**). The complexes **1–3** are oxidized by molecular iodine to $[M_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$, M = Rh, Pz = pz (**4**); M = Ir, Pz = pz (**5**), dmpz (**6**). Complexes **4–6** undergo halide abstraction with silver nitrate to form $[M_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(NO_3)_2(CO)_2]$, M = Rh, Pz = pz (**7**); M = Ir, Pz = pz (**8**), dmpz (**9**). Complexes **2** and **3** react with mercury(II) chloride in 1:1 mole ratio to give the iridium(III)–iridium(I) complexes $[Ir_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(\mu\text{-HgCl})Cl(CO)_2]$, Pz = pz (**10**), dmpz (**11**) resulting from oxidative addition of $HgCl_2$ to one metal centre. Interaction of the mixed oxidation state complexes **10** and **11** with mercury(II) chloride affords the diiridium(II) compounds $[Ir_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})Cl_2(CO)_2]$, Pz = pz (**12**), dmpz (**13**).

Introduction

Considerable interest has recently been shown in binuclear complexes containing rhodium or iridium centres in close proximity. Among those, binuclear compounds with two *cis*-binucleating nitrogen donor atoms (e.g. pyrazolate [1–3] or triazolate [4–6] type ligands) or two *cis*-thiolate bridges [7–10] have been reported. On the other hand, binuclear compounds with two *trans*-μ-bis(diphenylphosphino) methane (dppm) ligands have been thoroughly investigated [11–13].

As part of our studies concerning the preparation and properties of binuclear complexes containing the $M(\mu\text{-az})(\mu\text{-X})M$ framework, where M is either rhodium or iridium, az an azolate type ligand and X an anion such as Cl, OH, N_3, we have recently synthesized the binuclear complexes of general formulae $[M_2(\mu\text{-pz})(\mu\text{-SBu}^t)(COD)_2]$ (M = Rh or Ir, pz = pyrazolate) [14, 15].

In this paper we report the preparation and reactivity of binuclear rhodium–rhodium or iridium–iridium complexes having the '$M(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})M$' core. In these complexes the two metal centres are connected by a triple bridge formed by a pyrazolate group, a t-butylthiolate ligand and a bis(diphenylphosphino)methane group.

Experimental

Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer. ^1H and ^{31}P NMR spectra were carried out in $CDCl_3$ solution at room temperature on a Varian XL 200 spectrometer. All preparations were carried out under nitrogen on a vacuum line using Schlenk techniques. Solvents were purified by standard methods prior to use. The reactants were of commercial origin and used without further purification. The complexes $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(COD)_2]$ and $[Ir_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(COD)_2]$, Pz = pz, dmpz, were prepared according to literature methods [14, 15].

Preparation of $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ *(1)*

$[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(COD)_2]$ (300 mg, 0.518 mmol) was dissolved in dichloromethane (15 ml) and dry carbon monoxide was bubbled through the solution for 30 min at room temperature. Then the CO flow was discontinued and a solution of bis(diphenylphosphino)methane (dppm), (199.3 mg,

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0.532 mmol) in dichloromethane (15 ml) was added. The reaction solution was stirred vigorously for 30 min. The volume was reduced to *c*. 2 ml and 10 ml of diethyl ether was slowly added. The solid was collected by filtration, washed with diethyl ether and vacuum-dried; yield: 291 mg (78%).

Preparation of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ *(2)*

The complex was prepared by the procedure described for $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ from $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(COD)_2]$ (403.1 mg, 0.532 mmol) and bis(diphenylphosphino)methane (dppm), (204.6 mg, 0.532 mmol). A total of 455 mg (87%) of the complex was obtained.

Preparation of $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ *(3)*

The complex was prepared by the procedure described for $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ from $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(COD)_2]$ (406.1 mg, 0.515 mmol) and bis(diphenylphosphino)methane (dppm), (198.2 mg, 0.515 mmol). A total of 434 mg (83%) of the complex was obtained.

Preparation of $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$ *(4)*

To a solution of $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ (100 mg, 0.124 mmol) in dichloromethane (20 ml) was added the stoichiometric amount of iodine (31.6 mg, 0.124 mmol). The progress of the reaction was followed by IR spectra. After 1 h stirring, the solvent was evaporated off to *c*. 3 ml and diethyl ether (10 ml) was added. The resulting precipitate was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 93 mg (71%).

Preparation of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$ *(5)*

This complex was prepared by the procedure described for $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$ from $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ (100 mg, 0.101 mmol) and iodine (25.8 mg, 0.101 mmol). A total of 86 mg (68%) of the complex was obtained.

Preparation of $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$ *(6)*

The complex was prepared by the procedure described for $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$ from $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ (100 mg, 0.098 mmol) and iodine (25.0 mg, 0.098 mmol). A total of 91 mg (73%) of the complex was obtained.

Preparation of $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(NO_3)_2(CO)_2]$ *(7)*

To a solution of $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$ (100 mg, 0.094 mmol) in acetone (15 ml) was added Ag NO_3 (32.2 mg, 0.189 mmol) in 5 ml of the same solvent. The resulting suspension was stirred, in the absence of light, for 30 min and the AgI formed was filtered off. Partial evaporation of the filtrate, under reduced pressure, and addition of diethyl ether (10 ml) gave a solid which was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 51 mg (58%).

Preparation of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(NO_3)_2(CO)_2]$ *(8)*

The complex was prepared by the procedure described for $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(NO)_3)_2(CO)_2]$ from $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$ (100 mg, 0.080 mmol) and Ag NO_3 (27.4 mg, 0.161 mmol). A total of 64.5 mg (72%) of the complex was obtained.

Preparation of $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(NO_3)_2(CO)_2]$ *(9)*

The complex was prepared by the procedure described for $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(NO_3)_2(CO)_2]$ from $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$ (100 mg, 0.079 mmol) and $AgNO_3$ (26.8 mg, 0.158 mmol). A total of 61 mg (67%) of the complex was obtained.

Preparation of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(HgCl)Cl(CO)_2]$ *(10)*

Solid $HgCl_2$ (55.2 mg, 0.203 mmol) was added to a solution of $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ (200 mg, 0.203 mmol) in dichloromethane (15 ml). The mixture was stirred for 1 h and the resulting solution was filtered through kieselguhr. Then the solvent was evaporated off under reduced pressure to *c*. 1 ml. Addition of diethyl ether (10 ml) led to the precipitation of a solid which was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 166 mg (65%).

Preparation of $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(HgCl)Cl(CO)_2]$ *(11)*

The complex was prepared by the procedure described for $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(HgCl)Cl(CO)_2]$ from $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ (100 mg, 0.098 mmol) and $HgCl_2$ (26.8 mg, 0.098 mmol). A total of 90 mg (71%) of the complex was obtained.

Preparation of $[\mathrm{Ir_2}(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})\mathrm{Cl_2(CO)_2}]$ *(12)*

A solution of $[\mathrm{Ir_2}(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})\mathrm{(HgCl)Cl(CO)_2}]$ (255 mg, 0.203 mmol) in dichloromethane (15 ml) was allowed to react with mercury(II) chloride (55.2 mg, 0.203 mmol). After 1 h the initial compound $[\mathrm{Ir_2}(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})\mathrm{(HgCl)Cl(CO)_2}]$ was consumed. The resulting suspension was filtered through kieselguhr to remove the mercury(I) chloride, and the filtrate was concentrated under reduced pressure to *c*. 1 ml. Addition of diethyl ether (10 ml) gave a yellow solid which was isolated by filtration, washed with diethyl ether and dried *in vacuo*. Yield 129 mg (60%).

This complex can be prepared by reaction of $[\mathrm{Ir_2}(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})\mathrm{(CO)_2}]$ (200 mg, 0.203 mmol) with $\mathrm{HgCl_2}$ (110.4 mg, 0.406 mmol).

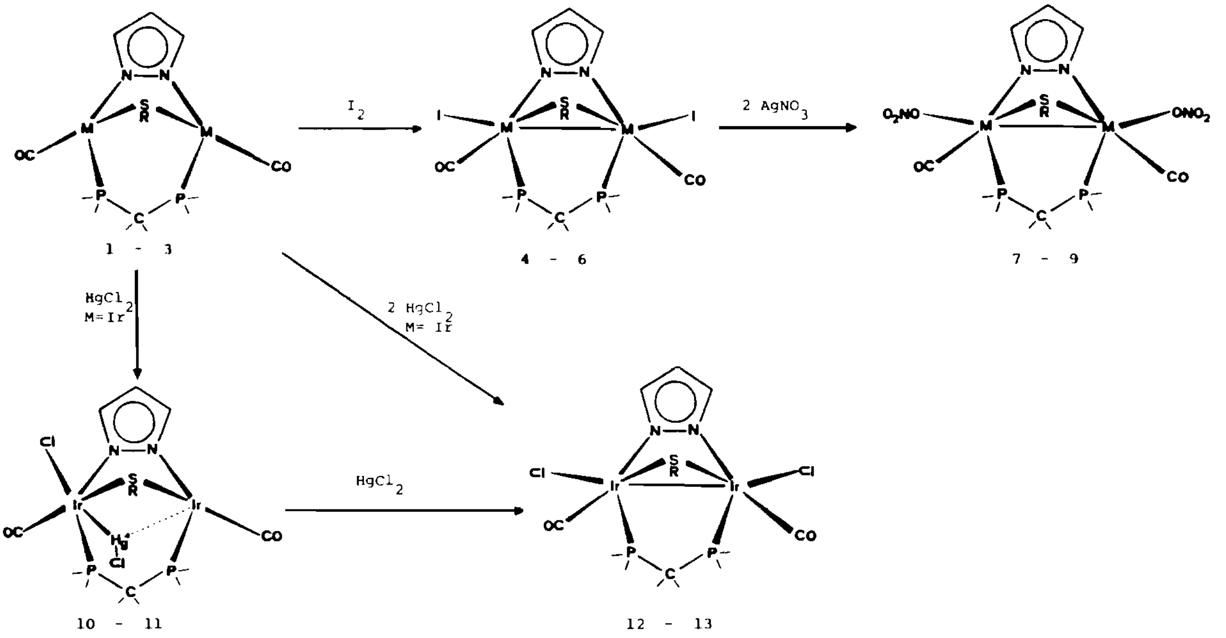
Preparation of $[\mathrm{Ir_2}(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})\mathrm{Cl_2(CO)_2}]$ *(13)*

The complex was prepared by the procedure described for $[\mathrm{Ir_2}(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})\mathrm{Cl_2(CO)_2}]$ from $[\mathrm{Ir_2}(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})\mathrm{(HgCl)Cl(CO)_2}]$ (127 mg, 0.098 mmol) and $\mathrm{HgCl_2}$ (26.8 mg, 0.098 mmol), or from $[\mathrm{Ir_2}(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})\mathrm{(CO)_2}]$ (100 mg, 0.098 mmol) and $\mathrm{HgCl_2}$ (53.7 mg, 0.186 mmol). A total of 75 mg (70%) of the complex was obtained.

Results and discussion

Bubbling carbon monoxide at atmospheric pressure through a dichloromethane solution of $[\mathrm{Rh_2}(\mu\text{-pz})(\mu\text{-SBu}^t)\mathrm{(COD)_2}]$ for a few minutes gave an intermediate (presumably $[\mathrm{Rh_2}(\mu\text{-pz})(\mu\text{-SBu}^t)\mathrm{(CO)_4}]$) which was not isolated as a solid. Addition of a dichloromethane solution of bis(diphenylphosphino)methane (dppm) yields in essentially quantitative yield $[\mathrm{Rh_2}(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})\mathrm{(CO)_2}]$ (**1**). The iridium complexes $[\mathrm{Ir_2}(\mu\text{-Pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})\mathrm{(CO)_2}]$, Pz = pz (**2**), dmpz (**3**) were prepared similarly starting from $[\mathrm{Ir_2}(\mu\text{-Pz})(\mu\text{-SBu}^t)\mathrm{(COD)_2}]$, Pz = pz or dmpz, respectively. The formulation of these complexes is substantiated by microanalytical results, molecular weight measurements and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectral data. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **1** shows a symmetric multiplet (AA'XX') spin system with δ P at 26.2 ppm [16]. The separation between the two major peaks (^1J(Rh–P) + ^xJ(Rh–P)) is 130 Hz. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **2** shows a singlet at δ 14.6 ppm indicating a symmetrical species in which the two phosphorus nuclei are chemically equivalent, in addition a singlet appears in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **3** ($\delta = 13.3$ ppm).

On the basis of these data, compounds **1–3** are assigned to structure represented in Scheme 1. In these triply heterobridged complexes the two metal atoms are connected by one dppm group, one exobidentate pyrazolate ligand and one t-buthylthiolate anion. In this context, it is interesting to note that the reaction of $[\mathrm{Rh_2}(\mu\text{-pz})_2\mathrm{(CO)_4}]$ with bis-



Scheme 1.

(diphenylphosphine)methane (Rh:dppm = 2:1) in several solvents results in the displacement of one pyrazolate group with formation of $[Rh_2(\mu\text{-pz})(\mu\text{-dppm})_2(CO)_2]^+$ cations [17].

Complexes **1**–**3** react readily with an equimolar amount of molecular iodine to give **4**–**6**, respectively, which on the basis of elemental analysis, infrared and NMR spectral data are formulated as the metal(II)–metal(II) complexes $[M_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$ (M = Rh, Pz = pz (**4**); M = Ir, Pz = pz (**5**); M = Ir, Pz = dmpz (**6**)) (Scheme 1). The presence of only a single terminal ν(CO) band in each case at 2055, 2040 and 2040 cm^{-1}, respectively, suggests that single symmetrical derivatives are formed. The ν(CO) bands of the oxidation products are shifted towards higher frequencies relative to those for the parent compounds, the observed shifts ($\Delta\nu$(CO) = 60 (**4**), 50 (**5**) and 55 (**6**) cm^{-1}) support the formulation of the compounds as dimetal(II) derivatives. Further confirmation of a symmetrical structure for **4**–**6** comes from their $^{31}P\{^1H\}$ NMR spectra; the $^{31}P\{^1H\}$ NMR spectrum of **4** is a symmetric second order pattern very similar to that observed for **1** with δ P = 5.7 ppm; the separation between the two major peaks (^1J(Rh–P) + ^xJ(Rh–P)) reflects the change in the oxidation state of the metal centres, thus for complex **4** the two principal lines are separated by 84 Hz. Complexes **5** and **6** are characterized by a singlet in their $^{31}P\{^1H\}$ spectra at −24.9 and −23.1 ppm, respectively.

The terminal iodide ligands in the complexes $[M_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})I_2(CO)_2]$ (**4**–**6**) are labile and can be readily removed upon reaction with a variety of silver salts. When complexes (**4**–**6**) react with silver nitrate, orange (**7**, **9**) or yellow (**8**) complexes analyzing as $[M_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(NO_3)_2(CO)_2]$ M = Rh, Pz = pz (**7**); M = Ir, Pz = pz (**8**); M = Ir, Pz = dmpz (**9**) are obtained. Complexes **7**–**9** are non-conducting in dichloromethane solutions; this behaviour indicates coordination of the nitrate groups to the metal centres, in addition the $^{31}P\{^1H\}$ NMR spectra (Table 1) show that they have sym-

TABLE 1. Analytical and IR data for complexes **1**–**13**

Complex	Analysis: calc.(found)			IR data ν(C≡O)	^{31}P δ (ppm)	^1J(Rh–P) + ^xJ(Rh–P) (Hz)	Color
	C	H	N				
1	51.10 (50.88)	4.29 (4.77)	3.44 (3.49)	1995, 1985(sh)	26.2(m)	130	red
2	40.69 (40.31)	3.68 (3.48)	2.46 (2.84)	1990, 1970(sh)	14.6(s)		violet
3	42.25 (42.76)	3.72 (3.78)	2.57 (2.77)	1985, 1965(sh)	13.3(s)		violet
4	39.04 (38.66)	3.13 (2.95)	2.61 (2.65)	2055	5.7(m)	84	dark-brown
5	32.90 (33.01)	2.84 (2.68)	1.94 (2.26)	2040	−24.9(s)		yellow
6	33.91 (34.18)	3.03 (3.02)	1.96 (2.21)	2040	−23.1(s)		yellow
7	43.51 (44.07)	3.99 (3.58)	5.81 (6.04)	2065	8.2(m)	85	orange
8	37.01 (36.88)	3.34 (3.09)	4.89 (5.06)	2055	−15.2(s)		yellow
9	37.91 (38.09)	3.22 (3.37)	4.60 (4.93)	2050	−22.9(s)		pale-orange
10	32.76 (32.55)	3.22 (2.73)	1.99 (2.23)	2035, 2010			orange
11	33.71 (33.57)	2.98 (2.65)	2.18 (2.09)	2030, 2010	5.1(s), −26.8(s)		pale-orange
12	38.23 (38.74)	2.91 (3.25)	2.01 (2.65)	2035	−27.1(s)		yellow
13	39.96 (39.54)	3.53 (3.31)	2.58 (2.34)	2035	−26.8(s)		yellow

metrical forms. On the basis of the structures suggested for the precursors **4–6** complexes **7–9** are formulated as shown in Scheme 1.

Addition of mercury(II) chloride to a dichloromethane solution of $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(CO)_2]$ (**3**), at room temperature, caused the colour of the solution to change from yellow to red. Microanalytical and spectroscopic data for the orange solid isolated suggest the formation of $[Ir_2(\mu\text{-dmpz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(HgCl)Cl(CO)_2]$ (**11**). The IR spectrum of complex **11** presents two ν(CO) bands at 2030 and 2010 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum contains two singlets at 5.1 and −26.8 ppm. We have previously characterized, by X-ray methods, a related complex $[Rh_2(\mu\text{-pz})_2(\mu\text{-HgCl})Cl(CO)_2(PPh_3)_2]$ which shows a mercury atom asymmetrically bridging the two rhodium atoms [18]. On the basis of the above mentioned observations we suggest that complex **11** may also be interpreted as resulting from the oxidative addition of $HgCl_2$ to one iridium centre and simultaneous Lewis acid–base bonding between Hg and the other iridium atom (Scheme 1). Similarly, complex **2** reacts with $HgCl_2$ (Ir:Hg = 2:1) to form $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(HgCl)Cl(CO)_2]$ (**10**).

Attempts to prepare the diiridium(III) complexes $[Ir_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})(HgCl_2)_2(CO)_2]$ by reaction of a stoichiometric amount of mercury(II) chloride with complexes **10** or **11** results in the precipitation of mercury(I) chloride and formation of the diiridium(II) compounds $[Ir_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(\mu\text{-dppm})Cl_2(CO)_2]$, Pz = pz (**12**), Pz = dmpz (**13**) (Scheme 1). The $^{31}P\{^1H\}$ NMR spectra of complexes **12** and **13** show singlets at −27.1 and −26.8 ppm, respectively. As expected, the above mentioned diiridium(II) complexes **12** and **13** can be obtained by reaction of the diiridium(I) complexes **2** or **3** with mercury(II) chloride (Ir:Hg = 1:1).

Table 1 lists the analytical data for the isolated complexes. The various reactions mentioned above are summarized in Scheme 1.

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