Synthesis of Mononuclear *cis*-$M(C_6X_5)_2L_2$ or Binuclear $[M(\mu\text{-}L)(C_6X_5)_2]_2$ Complexes (M = Pd, Pt; X = F, Cl) Containing Neutral O- or S-donor Ligands L

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Abstract

Binuclear derivatives $[M(\mu\text{-}L)(C_6X_5)_2]_2$ (M = Pd, Pt; X = F, Cl; L = ONC_5H_4OMe-*p*, SC_4H_8, SMe_2, $SPPh_3$) are obtained by reacting *cis*-$M(C_6X_5)_2(OC_4H_8)_2$ with the corresponding ligands L (molar ratio 1:1). When the reactions are carried out in a 1:2 molar ratio the mononuclear derivatives *cis*-$M(C_6X_5)_2L_2$ (M = Pd, Pt; X = F, Cl; L = $OPPh_3$, ONC_5H_4OMe-*p*, SC_4H_8, SMe_2) are obtained. For L = $OPPh_3$ only the mononuclear complexes are isolated, while the binuclear derivatives are obtained when L = $SPPh_3$ for any molar ratio used. The binuclear derivatives can also be obtained by reacting *cis*-$M(C_6X_5)_2L_2$ with *cis*-$M(C_6X_5)_2(OC_4H_8)_2$ (molar ratio 1:1). The structures of these complexes are discussed on the basis of IR, ^1H and ^{19}F NMR data.

Introduction

Recently [1–3] we have reported the synthesis of *cis*-$M(C_6X_5)_2(OC_4H_8)_2$ complexes (M = Pd, Pt; X = F, Cl; OC_4H_8 = tetrahydrofuran), which are excellent precursors for the syntheses of some otherwise inaccessible novel complexes, since the neutral ligands can be easily displaced by CO [1, 2], PhC≡CPh [3], or *cis*-MX'_2(1,5-COD) [4] to give *cis*-dicarbonyl, *cis*-bisacetylene or halide (X') single-bridged tetranuclear derivatives of palladium or platinum.

Now we wish to report the use of the same precursors *cis*-$M(C_6X_5)_2(OC_4H_8)_2$ for the deliberate synthesis of binuclear complexes of the general formulae $[M(\mu\text{-}L)(C_6X_5)_2]_2$ (M = Pd, Pt; X = F, Cl), where the bridging ligand L is a neutral monodentate O- or S-donor. Palladium or platinum complexes of this type have hitherto been very scarce because of the lack of a general method leading to their preparation [5].

Results and Discussion

Synthesis of Binuclear $[M(\mu\text{-}L)(C_6X_5)_2]_2$ and Mononuclear cis-$M(C_6X_5)_2L_2$ Derivatives

Addition of the neutral ligands L to dichloromethane solutions of *cis*-$M(C_6X_5)_2(OC_4H_8)_2$ (1:1 ratio, eqn. (1)) leads to partial precipitation of the binuclear L-bridged derivatives. The yields can be improved by evaporating the solutions to small volume (see 'Experimental').

$$cis\text{-}M(C_6X_5)_2(OC_4H_8)_2 + L \longrightarrow \tfrac{1}{2}[M(\mu\text{-}L)(C_6X_5)_2]_2 + 2OC_4H_8 \quad (1)$$

L = SC_4H_8; M = Pd; X = F (**1**), Cl (**2**); M = Pt; X = F (**3**), Cl (**4**)

L = SMe_2; M = Pt; X = F (**5**)

L = $SPPh_3$; M = Pd; X = F (**6**); M = Pt; X = F (**7**)

L = ONC_5H_4OMe-*p*, M = Pd; X = F (**8**); M = Pt; X = F (**9**)

The use of a 1:2 molar ratio generally leads (eqn. (2)) to mononuclear derivatives *cis*-$M(C_6X_5)_2L_2$.

$$cis\text{-}M(C_6X_5)_2(OC_4H_8)_2 + 2L \longrightarrow cis\text{-}M(C_6X_5)_2L_2 + 2OC_4H_8 \quad (2)$$

L = SC_4H_8; M = Pd; X = F (**11**), Cl (**12**); M = Pt; X = F (**13**), Cl (**14**)

L = SMe_2; M = Pt; X = F (**15**)

L = $OPPh_3$; M = Pd; X = F (**16**), Cl (**17**); M = Pt; X = F (**18**)

L = ONC_5H_4OMe-*p*, M = Pd; X = F (**19**); M = Pt; X = F (**20**)

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The isolation of the mononuclear derivatives provides an alternative way for the synthesis of the binuclear complexes (eqn. (3))

$$cis\text{-}M(C_6X_5)_2(OC_4H_8)_2 + cis\text{-}M(C_6X_5)_2L_2 \longrightarrow [M(\mu\text{-}L)(C_6X_5)_2]_2 + 2OC_4H_8 \quad (3)$$

Some peculiarities have been observed: (i) $SPPh_3$ always forms the binuclear complexes (**6**, **7**) irrespective of the molar ratio used, probably owing to the very low solubility of both derivatives; (ii) $OPPh_3$ always forms the mononuclear complexes, for instance, $cis\text{-}M(C_6F_5)_2(OPPh_3)_2$ (M = Pd, Pt) are unreactive towards $cis\text{-}M(C_6F_5)_2(OC_4H_8)_2$ (eqn. (3)) and if the reaction is carried out in a solvent of higher boiling point (benzene instead of dichloromethane) to force the displacement of OC_4H_8, decomposition to metal takes place; (iii) all the above reactions

TABLE 1. Analytical results for the complexes **1**–**20**

Complex		C	H	N
1	$[Pd(\mu\text{-}SC_4H_8)(C_6F_5)_2]_2$	37.5 (37.4)	1.5 (1.5)	
2	$[Pd(\mu\text{-}SC_4H_8)(C_6Cl_5)_2]_2$	28.3 (27.7)	1.1 (1.2)	
3	$[Pt(\mu\text{-}SC_4H_8)(C_6F_5)_2]_2$	31.1 (30.7)	1.3 (1.2)	
4	$[Pt(\mu\text{-}SC_4H_8)(C_6Cl_5)_2]_2$	25.0 (24.6)	1.2 (1.0)	
5	$[Pt(\mu\text{-}SMe_2)(C_6F_5)_2]_2$	27.9 (28.4)	0.9 (1.0)	
6	$[Pd(\mu\text{-}SPPh_3)(C_6F_5)_2]_2$	48.5 (49.0)	2.2 (2.4)	
7	$[Pt(\mu\text{-}SPPh_3)(C_6F_5)_2]_2$	43.8 (43.4)	1.8 (1.9)	
8	$[Pd(\mu\text{-}ONC_5H_4OMe\text{-}p)(C_6F_5)_2]_2$	38.3 (38.2)	1.1 (1.3)	2.6 (2.5)
9	$[Pt(\mu\text{-}ONC_5H_4OMe\text{-}p)(C_6F_5)_2]_2$	32.6 (33.0)	1.0 (1.1)	2.0 (2.2)
10	$(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)_2Pt(C_6Cl_5)_2$	27.2 (27.5)	1.4 (1.2)	
11	$cis\text{-}Pd(C_6F_5)_2(SC_4H_8)_2$	38.8 (38.9)	2.5 (2.6)	
12	$cis\text{-}Pd(C_6Cl_5)_2(SC_4H_8)_2$	30.6 (30.7)	2.3 (2.1)	
13	$cis\text{-}Pt(C_6F_5)_2(SC_4H_8)_2$	33.9 (34.0)	2.2 (2.3)	
14	$cis\text{-}Pt(C_6Cl_5)_2(SC_4H_8)_2$	27.4 (27.6)	2.0 (1.9)	
15	$cis\text{-}Pt(C_6F_5)_2(SMe_2)_2$	30.1 (29.4)	1.9 (1.8)	
16	$cis\text{-}Pd(C_6F_5)_2(OPPh_3)_2$	57.6 (57.8)	2.9 (2.9)	
17	$cis\text{-}Pd(C_6Cl_5)_2(OPPh_3)_2$	49.2 (49.6)	2.8 (2.6)	
18	$cis\text{-}Pt(C_6F_5)_2(OPPh_3)_2$	52.6 (53.1)	2.8 (2.8)	
19	$cis\text{-}Pd(C_6F_5)_2(ONC_5H_4OMe\text{-}p)_2$	41.4 (41.1)	2.0 (2.0)	4.1 (4.1)
20	$cis\text{-}Pt(C_6F_5)_2(ONC_5H_4OMe\text{-}p)_2$	36.8 (37.0)	1.7 (1.8)	3.7 (3.6)

(eqns. 1–3) occur with stereoretention, i.e. the two C_6X_5 groups keep their *cis*-position in the coordination sphere of the metals (Pd or Pt).

Obviously, the reactions represented in eqn. (3) could be adequate for the synthesis of mixed derivatives by suitable combination of the reagents, provided that no rearrangement of ligands takes place. Both types of behaviour have been observed. For instance, a binuclear mixed pentachloropentafluorophenyl platinum derivative (**10**) has been isolated (eqn. (4))

$$cis\text{-}Pt(C_6Cl_5)_2(SC_4H_8)_2 + cis\text{-}Pt(C_6F_5)_2(OC_4H_8)_2 \longrightarrow (C_6Cl_5)_2Pt(\mu\text{-}SC_4H_8)_2Pt(C_6F_5)_2 + 2OC_4H_8 \quad (4)$$

but when the more labile palladium substrata are used, rearrangement processes take place; thus in the reaction between *cis*-$Pd(C_6Cl_5)_2(SC_4H_8)_2$ (**12**) and *cis*-$Pd(C_6F_5)_2(OC_4H_8)_2$ in CH_2Cl_2, the binuclear complex $[Pd(\mu\text{-}SC_4H_8)(C_6Cl_5)_2]_2$ (**2**) precipitates and $[Pd(\mu\text{-}SC_4H_8)(C_6F_5)_2]_2$ (**1**) can be isolated from the mother liquors. *cis*-$Pt(C_6Cl_5)_2(SC_4H_8)_2$ (**14**) also reacts with *cis*-$Pd(C_6F_5)_2(OC_4H_8)_2$ under similar conditions yielding $[Pt(\mu\text{-}SC_4H_8)(C_6Cl_5)_2]_2$ (**4**) and $[Pd(\mu\text{-}SC_4H_8)(C_6F_5)_2]_2$ (**1**).

Table 1 collects analytical results for complexes **1**–**20**. Neither the binuclear nor the mononuclear complexes are generally soluble enough in $CHCl_3$ to enable determination of their molecular weights, the only exception being *cis*-$Pd(C_6F_5)_2(SC_4H_8)_2$ (**11**), which gives 613 (calc. 617).

IR Spectra

IR absorptions of structural interest are collected in Table 2. All the complexes show bands indicating the *cis*-disposition of the two C_6X_5 groups linked to the metal atom. Pentafluorophenyl derivatives display two absorptions in the 800 cm^{-1} region due to the X-sensitive mode of the C_6F_5 group, whilst the pentachlorophenyl analogues show two absorptions in the 820–850 cm^{-1} region due to the X-sensitive mode of the C_6Cl_5 group and two absorptions due to ν(M–C) in the 620–635 cm^{-1} region [7]. The spectra of the mononuclear complexes *cis*-$M(C_6X_5)_2(OPPh_3)_2$ (**16**–**18**) show two absorptions in the 1150 cm^{-1} region due to ν(P=O), decreased respective to the free ligand because of the lowering of the P–O bond order [8] and split as a consequence of the coupling of both ν(P–O) vibrations via the coordination to the same metal centre, thereby producing separate symmetric and asymmetric stretching modes [8], both IR active for the *cis* isomer. A similar behaviour is exhibited by complexes **19** and **20**. Two bands due to ν_{sym}(N–O) and ν_{asym}(N–O) (both IR active for

TABLE 2. Relevant IR data (cm^{-1}) for the complexes **1**–**20**

Complex		X-sensitive mode	ν(M–C)	Other
1	$[Pd(\mu\text{-}SC_4H_8)(C_6F_5)_2]_2$	790s, 781s		
2	$[Pd(\mu\text{-}SC_4H_8)(C_6Cl_5)_2]_2$	840w, 832sh	621m, 615m	
3	$[Pt(\mu\text{-}SC_4H_8)(C_6F_5)_2]_2$	806s, 799s		
4	$[Pt(\mu\text{-}SC_4H_8)(C_6Cl_5)_2]_2$	845sh, 840w	633m, 627m	
5	$[Pt(\mu\text{-}SMe_2)(C_6F_5)_2]_2$	810s, 803s		
6	$[Pd(\mu\text{-}SPPh_3)(C_6F_5)_2]_2$	792s, 781s		575vs[a]
7	$[Pt(\mu\text{-}SPPh_3)(C_6F_5)_2]_2$	804s, 793s		565vs[a]
8	$[Pd(\mu\text{-}ONC_5H_4OMe\text{-}p)(C_6F_5)_2]_2$	803s, 796s		1201vs[b]
9	$[Pt(\mu\text{-}ONC_5H_4OMe\text{-}p)(C_6F_5)_2]_2$	818s, 808s		1189s, 1183s[b]
10	$(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)_2Pt(C_6Cl_5)_2$	841w, 834sh, 806m, 748m	626 broad	
11	*cis*-$Pd(C_6F_5)_2(SC_4H_8)_2$	793s, 783s		
12	*cis*-$Pd(C_6Cl_5)_2(SC_4H_8)_2$	833w, 827w	611m, 606m	
13	*cis*-$Pt(C_6F_5)_2(SC_4H_8)_2$	800s, 790s		
14	*cis*-$Pt(C_6Cl_5)_2(SC_4H_8)_2$	840w, 832w	632sh, 624m	
15	*cis*-$Pt(C_6F_5)_2(SMe_2)_2$	803s, 790s		
16	*cis*-$Pd(C_6F_5)_2(OPPh_3)_2$	810s, 795s		1167s, 1138s[c]; 1118s[d]
17	*cis*-$Pd(C_6Cl_5)_2(OPPh_3)_2$	842w, 836sh	627m, 618m	1160s, 1146s[c]; 1120s[b]
18	*cis*-$Pt(C_6F_5)_2(OPPh_3)_2$	819s, 805s		1150s, 1129s[c]; 1118s[d]
19	*cis*-$Pd(C_6F_5)_2(ONC_5H_4OMe\text{-}p)_2$	800s, 789s		1201s, 1192s[b]
20	*cis*-$Pt(C_6F_5)_2(ONC_5H_4OMe\text{-}p)_2$	812s, 802s		1194s, 1187s[b]

[a] ν(P–S); ν(P=S) in $SPPh_3$ 637. [b] ν(N–O); ν(N–O) in ONC_5H_4OMe-*p* 1213 [6]. [c] ν(P=O) in $OPPh_3$ 1184. [d] Internal absorptions of $OPPh_3$, 1118 in the free ligand.

the *cis* isomer) and slightly shifted towards lower energies than in the free ligand are observed in the 1190–1200 cm^{-1} region, which is in accordance with other reported examples [9].

Complexes **6** and **7**, containing bridging $SPPh_3$ show a strong absorption due to ν(S=P) shifted towards lower energies with respect to the free ligand ($\Delta\nu$ 62 (**6**), 72 (**7**) cm^{-1}). This shift is actually greater than that observed for other palladium or platinum derivatives containing terminal $SPPh_3$ ($\Delta\nu$ 47 cm^{-1}) [10], showing that the S–P bond is weaker when the ligand is acting as a bridge.

While complex **8** shows a single strong absorption at 1201 cm^{-1} assignable to ν(N–O), complex **9** shows two strong and very close absorptions (1189, 1183 cm^{-1}) due to ν(N–O). It is possible that the observed splitting arises from crystal effects, but unfortunately the very low solubility of complex **9** in non-donor solvents precludes the verification of this hypothesis. As may be seen from Table 2, $\Delta\nu$ in mononuclear (**19**, **20**) or binuclear (**8**, **9**) derivatives is small, which is consistent with the idea that in the case of ONC_5H_4OMe-*p*, as a consequence of the donor nature of the *p*-MeO groups, the N–O bond in the free ligand is weaker than in the unsubstituted C_5H_5NO [11].

Some ^1H and ^{19}F NMR Spectra

Although the structure of these complexes can be established from the IR data, the ^1H and ^{19}F NMR spectra of some complexes have been studied. ^1H NMR of *cis*-$Pt(C_6F_5)_2(SC_4H_8)_2$ (**13**) shows two multiplets centred at 1.86 and 3.05 ppm; when the signal at 1.86 ppm is irradiated, the signal at 3.05 ppm due to the CH_2 groups attached to the S atom, appears as a singlet with platinum satellites ($^3J_{Pt-H}$ 33.4 Hz); the intensities of the three signals (1:4:1) are in agreement with the presence of the SC_4H_8 groups bonded to only one platinum centre. The ^1H NMR of *cis*-$Pt(C_6F_5)_2(SMe_2)_2$ (**15**) shows a singlet (2.3 ppm) with the corresponding platinum satellites ($^3J_{Pt-H}$ 32.5 Hz; 1:4:1). The ^{19}F NMR spectra of complexes **13** and **15** display the following signals: complex **13**, δ –119.9 (d, F_o, $^3J_{Pt-F}$ 406 Hz), –161.8 (m, F_m), –164.2 (m, F_p) ppm; complex **15**, δ –120.3 (d, F_o; $^3J_{Pt-F}$ 402 Hz), –161.8 (m, F_p), –164.2 (m, F_m) ppm, indicating that in each case both C_6F_5 groups are equivalent.

In non-donor solvents the binuclear derivatives are not soluble enough for NMR studies and in fact only $[Pt(\mu\text{-}SMe_2)(C_6F_5)_2]_2$ (**5**) in CD_2Cl_2 could be studied. The bridging nature of a ligand group containing some active nuclei (H) can be established by examination of ^{195}Pt satellites, since if the ligand is attached to two platinum atoms, a 1:8:18:8:1 quintet with spacing of $1/2J_{Pt-H}$ should be observed because of the increased probability of ^{195}Pt influence. The ^1H NMR resonance of the CH_3 group in complex **5** confirms the presence of the SMe_2 as a bridging ligand and although not all the five peaks can be observed, the area ratios of the three observed ones are 8:18:8; δ 2.78 (s, CH_3; $^3J_{Pt-H}$ 36.5 Hz) ppm. The ^{19}F NMR spectrum of complex **5** δ –119.38 (d, F_o; $^3J_{Pt-F}$ 403 Hz), –151.09 (m, F_p), –165.65 (m, F_m) ppm, indicates that all C_6F_5 groups are equivalent.

Experimental

C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (4000–200 cm^{-1}), using Nujol mulls between polyethylene sheets. Conductivities were measured with a Philips PW 9509 conductimeter. Molecular weights were measured in approx. 10^{-3} m solution in $CHCl_3$ using the isopiestic method on a Knauer apparatus. ^1H and ^{19}F NMR spectra were recorded on a Varian XL 200 spectrometer (200 MHz for ^1H) in $CDCl_3$ (**13** and **15**) or CD_2Cl_2 (**5**).

cis-$Pt(C_6F_5)_2(OC_4H_8)_2$ and *cis*-$Pt(C_6Cl_5)_2(OC_4H_8)_2$ were prepared as described elsewhere [2]. The analogous palladium derivatives were prepared in a similar way, using $[NBu_4]_2[Pd(\mu\text{-}Cl)(C_6F_5)_2]_2$ [12] or $[NBu_4]_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$ [13] as starting materials {*cis*-$Pd(C_6F_5)_2(OC_4H_8)_2$, 90% yield; *cis*-$Pd(C_6Cl_5)_2(OC_4H_8)_2$, 80% yield}.

Syntheses of cis-$M(C_6X_5)_2L_2$ (M = Pd, Pt, X = F, Cl; L = SC_4H_8, SMe_2, $OPPh_3$, ONC_5H_4OMe-p) (11–20)

cis-$Pd(C_6F_5)_2(SC_4H_8)_2$ (11)

To a solution of 0.407 g (0.80 mmol) of *cis*-$Pd(C_6F_5)_2(OC_4H_8)_2$ in 20 ml of CH_2Cl_2, was added 0.142 ml (1.6 mmol; molar ratio 1:2) of SC_4H_8, and the solution was stirred at room temperature for 30 min. Evaporation to ~5 ml and addition of 10 ml of CH_3OH yields **11** (0.26 g, 60% yield), which was washed with n-hexane.

Complexes **12–20** were obtained similarly as detailed in Table 3.

Syntheses of the Binuclear Complexes 1–10

(a) [M(μ-$SPPh_3$)$(C_6F_5)_2]_2$, (M = Pd (6), Pt (7))

M = Pd (6). To a solution of 0.159 g (0.27 mmol) of *cis*-$Pd(C_6F_5)_2(OC_4H_8)_2$ in 20 ml of CH_2Cl_2, was added 0.160 g (0.54 mmol) of $SPPh_3$. A white precipitate was formed almost immediately, which was filtered and washed with n-hexane. The yield can be improved by evaporation of the mother liquours to ~5 ml and addition of ~10 ml n-hexane (total yield: 0.16 g, 90%).

The platinum derivative **7** can be obtained in a similar way: 0.15 g (0.223 mmol) of *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ and 0.065 g (0.223 mmol) of $SPPh_3$ render 0.16 g of **7** (86% yield).

TABLE 3. Experimental conditions for the preparation of complexes **11**–**20**

Complex	Substrate 1[a] (g) (mmol)	Ligand[b] (g) (mmol)	Yield (%)
11	0.47 (0.80)	0.14 (1.6)	60[d]
12	0.67 (0.89)	0.16 (1.8)	55[d]
13	0.87 (1.3)	0.23 (2.6)	76[d]
14	0.13 (0.16)	0.03 (0.3)	80[d]
15	0.20 (0.3)	0.04 (0.7)	67[e]
16	0.14 (0.24)	0.13 (0.5)	68[e]
17[c]	0.15 (0.20)	0.11 (0.4)	63[e]
18	0.20 (0.30)	0.16 (0.6)	85[d]
19	0.10 (0.17)	0.04 (0.3)	88[f]
20	0.20 (0.30)	0.07 (0.6)	89[f]

[a] *cis*-$M(C_6X_5)_2(OC_4H_8)_2$. [b] L = SC_4H_8, SMe_2, $OPPh_3$, ONC_5H_4OMe-*p*. [c] The reaction was carried out in diethyl ether, 20 ml. [d] The complexes were obtained by evaporating the CH_2Cl_2 solution to 5 ml and adding CH_3OH. [e] Obtained by evaporating the solution to 5 ml and adding n-hexane. [f] The solution was evaporated to dryness and the residue washed with n-hexane (**19**) or water (**20**).

(b) $[M(\mu\text{-}L)(C_6X_5)_2]_2$, (M = Pd, Pt; L = SC_4H_8, SMe_2) 1–5

Complex 1 (M = Pd; X = F) was obtained as follows. 0.256 g (0.43 mmol) of **11** was added to a solution of 0.28 g (0.41 mmol) of *cis*-$Pd(C_6F_5)_2(OC_4H_8)_2$ in 15 ml CH_2Cl_2, and the mixture was stirred at room temperature for 45 min. The precipitation of complex **1** takes place immediately, but the yield can be improved by evaporating to 5 ml. The resulting product was washed with Et_2O (0.35 g, 82% yield).

Working under similar conditions, complexes **2**–**5** were obtained.

2: 0.17 g (0.223 mmol) of **12** and 0.15 g (0.223 mmol) *cis*-$Pd(C_6Cl_5)_2(OC_4H_8)_2$ rendered **2**, which was washed with 3 × 5 ml of boiling CH_2Cl_2 (0.19 g, 63% yield).

3: 0.16 g (0.23 mmol) of **13** and 0.16 g (0.24 mmol) *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ gave 0.22 g of **3** (78% yield).

4: 0.19 g (0.22 mmol) of **14** and 0.15 g (0.22 mmol) of *cis*-$Pt(C_6Cl_5)_2(OC_4H_8)_2$ produced 0.22 g of **4** (65% yield).

5: 0.10 g (0.15 mmol) of **15** and 0.10 g (0.15 mmol) of *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ gave 0.155 g of **5** (86% yield).

(c) $M(\mu\text{-}ONC_5H_4OMe\text{-}p)(C_6F_5)_2]_2$ {M = Pd (8), Pt (9)}

8: 0.028 g (0.223 mmol) of *p*-methoxypyridine-*N*-oxide was added to 0.13 g (0.223 mmol) of *cis*-$Pd(C_6F_5)_2(OC_4H_8)_2$ in 10 ml of CH_2Cl_2, and the resulting solution was stirred at room temperature for 1 h. By evaporating to ~5 ml and adding ~10 ml of n-hexane, 0.095 g of **8** (washed with n-hexane) were obtained (75% yield).

9 was prepared by the same procedure. *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$, 0.176 g (0.248 mmol); ONC_5H_4OMe-*p*, 0.031 g (0.248 mmol); 0.108 g of **9** (67% yield).

(d) $(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)_2Pt(C_6Cl_5)_2$ (10)

To a solution of 0.117 g (0.17 mmol) of *cis*-$Pt(C_6F_5)_2(OC_4H_8)_2$ in 30 ml of CH_2Cl_2, 0.213 g (0.17 mmol) of **14** was added and the mixture was stirred at room temperature for 20 min. The resulting solution was evaporated to ~10 ml and 20 ml of CH_3OH were added to precipitate 0.1 g of **10**. By concentrating the mother liquors to ~10 ml further 0.08 g of **10** were obtained. Total yield 74%.

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