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3,5-dichlorotrifluorophenyl complexes, aryl derivatives with simple ^{19}F NMR structural probes. The synthesis of general precursors for Pd- and Pt complexes [1]

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Abstract

High yield methods for the synthesis of *cis*-[MR_2(COD)] (M = Pd, Pt; R = 3,5-$C_6Cl_2F_3$), *cis*-[$MR_2(THF)_2$] (M = Pd; Pt), *trans*-[PdR_2L_2] (L = tht; SMe_2), *trans*-[$PtR_2(SMe_2)_2$], and [$M_2(\mu$-Cl)$_2R_2L_2$] (M = Pd, L = NCPh, tht, SMe_2; M = Pt, L = tht) are reported. These complexes are general precursors for the preparation of other complexes containing *cis*-MR_2, *trans*-MR_2 and MClR moieties in almost quantitative yields. Thus, by displacement of COD, THF, tht or SMe_2 by other ligands, almost any isomer of any complex with one or two aryl rings can be prepared. The ^{19}F NMR spectra of these complexes are simple compared to those of other polyfluorophenyl groups, and some examples of the spectral advantages of this partially fluorinated ligand are given. © 1998 Elsevier Science S.A.

Keywords: 3,5-dichlorotrifluorophenyl complexes; ^{19}F NMR spectra; Pd- and Pt complexes

1. Introduction

Haloaryl ligands confer extra stability to the C–M bond and consequently have been widely used to prepare organometallic complexes of palladium and platinum. Among them, C_6F_5 is the most extensively used and has made possible the isolation of many new structural types of complexes [1–3]. However, other symmetrical polyfluorophenyl ligands are little represented in the literature [4–7].

The advantages of ^{19}F NMR spectroscopy for characterization and mechanistic studies, using fluoroaryl complexes as models of aryl complexes, have been discussed for C_6F_5 in some previous papers. For instance, it greatly facilitates the isolation and investigation of intermediates and products formed by insertion of one double bond of a diene into a Pd–C_6F_5 bond [8–11]. It is also of great help in the recognition and interpretation of fluxional processes, including real or apparent aryl rotation and dissociative or associative processes occurring on palladium [12,13].

In the course of mechanistic investigations on pentafluorophenyl complexes of palladium and platinum, we became interested in the synthesis of analogous stable polyfluorophenyl complexes with more simple but not less informative ^{19}F NMR spectra that would further facilitate these spectroscopic studies and interpretation, as well as computer simulations. This directed our attention to the 3,5-dichlorotrifluorophenyl ligand. Moreover, the availability of complexes with very similar but distinguishable R groups, such as 3,5-dichlorotrifluorophenyl and pentafluorophenyl, would allow mechanistic studies to be made involving R or ligand exchange.

In this paper, we report the synthesis of general precursors containing MR_2 or MRX moieties (X = halide; M = Pd, Pt; R = 3,5-$C_6Cl_2F_3$) stabilized with easily displaceable ligands (e.g., THF, PhCN, tht, SMe_2) or easily removable halides. From these precursors specific complexes are easily obtained. We also illustrate

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[1] Dedicated to Professor Peter Maitlis on the occasion of his 65th birthday. Olé, Peter.

with examples some of the spectral advantages of the use of this partially fluorinated ligand compared to C_6F_5.

2. Results

The reaction of equimolar amounts of 1,3,5-$C_6Cl_3F_3$ (RCl) and Li^{n}Bu in dry diethyl ether at −78°C gives the organolithium reagent LiR which has been used directly to arylate several palladium and platinum compounds. The reaction conditions, products and yields are listed in Table 1. The results obtained are similar to those previously described for C_6F_5 and C_6Cl_5 [2,14]. However, it must be noted that: (a) Arylation of *cis*-[MCl_2(COD)] (M = Pd, Pt) which affords the white air-stable complexes *cis*-[MR_2(COD)] (M = Pd, **1a**; Pt, **1b**) in high yields is an excellent alternative method (not used previously for C_6F_5 or similar ligands) to prepare many complexes containing M–R bonds; (b) $(NBu_4)_2[PdR_4]$ (**2a**) is accessible in 93% yield from $(NBu_4)_2[Pd_2Br_6]$ using only a slight excess of LiR (molar ratio 1:8.5) in contrast with the results reported for LiC_6F_5 (ratio 1:20, 64%) [15], or LiC_6Cl_5 (ratio 1:14, 64%) [16]; and (c) the products obtained from the reactions of [MCl_2L_2] (M = Pd, Pt; L = tht, SMe_2) and LiR are mixtures of *cis*- and *trans*-[MR_2L_2] (M = Pd, **4a**–**7a**, Pt, **4b**–**7b**) with variable ratios. The isomerization process for these complexes is slow (unnoticeable for Pt) and separation of *cis*- and *trans* isomers can be achieved using fractional crystallization and column chromatography as described in Section 5.

The products listed in Table 1 can be used to prepare other complexes containing MR or MRX moieties, as shown in Scheme 1.

2.1. Complexes with two R groups bonded to the metal center

The complexes *cis*-[MR_2(COD)] (M = Pd, **1a**; Pt, **1b**) can be transformed into *cis*-[$MR_2(THF)_2$] (M = Pd, **8a**; Pt, **8b**; THF = tetrahydrofuran), which contain two neutral ligands more easily displaceable, in two steps: the substitution of COD for halide gives the anionic complexes $[M_2(\mu\text{-}X)_2R_4]^{2-}$ (M = Pd, X = Br, **9a**; M = Pt, X = I, **9b**), isolated as their $(NBu_4)^+$ salts. Subsequent treatment of these with $AgClO_4$ (1:2 molar ratio) in THF under anhydrous conditions leads to *cis*-[$MR_2(THF)_2$]. These compounds are not very stable and must be stored in the solid state at −20°C [17,18]. The Pd complex is particularly unstable and the use of *cis*-[$PdR_2(NCPh)_2$] (**11a**) as storable precursor is recommended.

Alternatively $(NBu_4)_2[M_2(\mu\text{-}Cl)_2R_4]$ (M = Pd, **10a**; Pt, **10b**) can be used as starting materials. They are prepared in good yield by reaction of $(NBu_4)_2[MR_4]$ (M = Pd, **2a**; Pt, **2b**) with HCl (1:2 molar ratio) in a methanol/acetone mixture, although half of the R groups are lost as RH in this operation. For M = Pd, arylation of $PdCl_2$ with **2a** (1:1 molar ratio) in refluxing acetone gives **10a** in 80% yield, saving the waste of the valuable fluorinated material as RH in the previous method. The reaction between $(NBu_4)_2${*trans*-[$PtCl_2R_2$]} (**3b**) and $AgNO_3$ or $AgClO_4$ (1:2 molar ratio) in acetonitrile followed by addition of a large excess of SMe_2 causes AgCl precipitation and formation of *trans*-[$PtR_2(SMe_2)_2$] (**7b**).

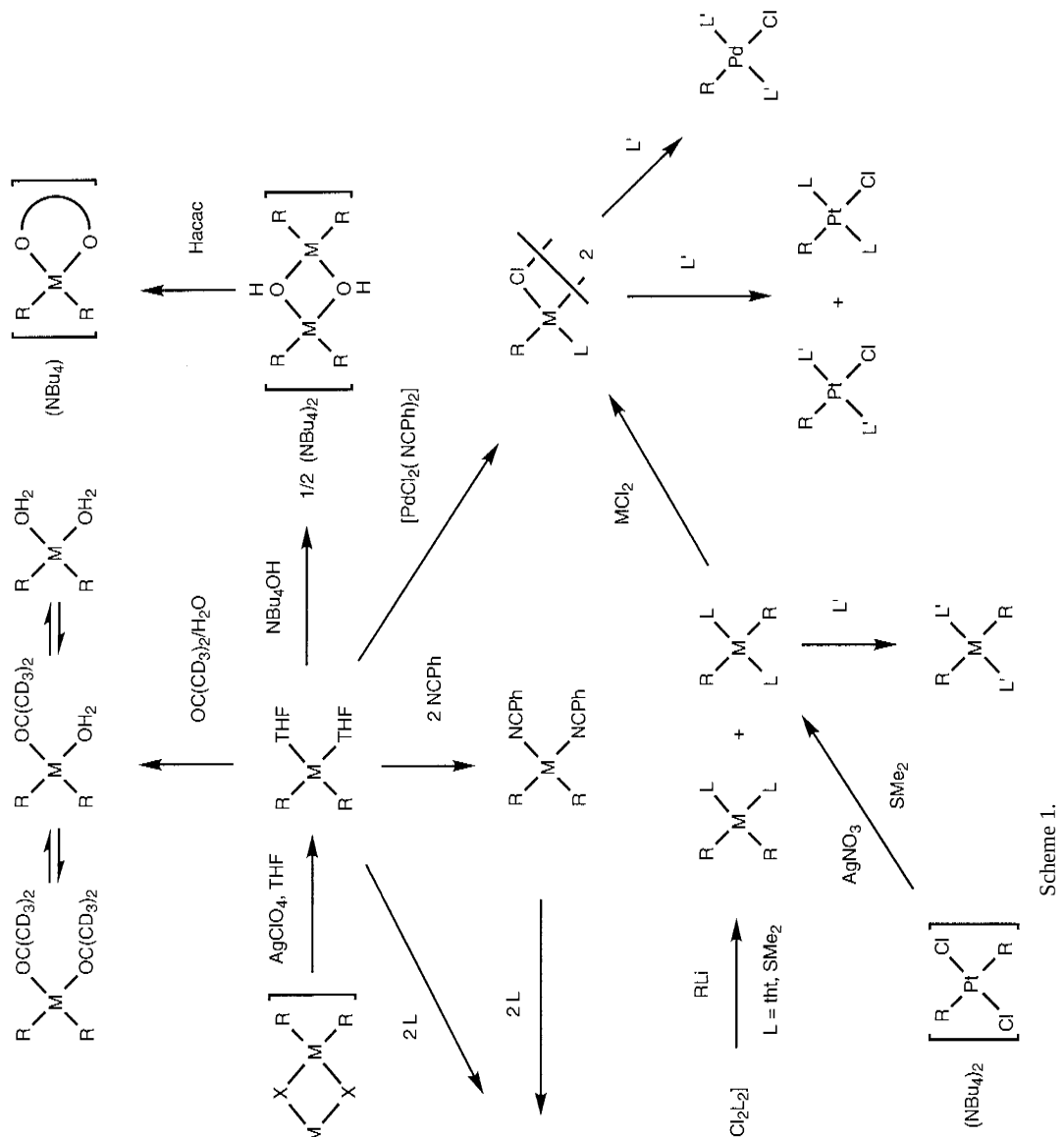
All these complexes, *cis*-[MR_2(COD)] (**1a**, **1b**), *cis*-[$MR_2(THF)_2$] (**8a**, **8b**), *trans*-[PdR_2L_2] (L = tht, **5a**; SMe_2, **7a**) and *trans*-[$PtR_2(SMe_2)_2$] (**7b**) provide very simple entries to many *cis*- and *trans*-[MR_2L_2] by direct substitution of COD, THF, tht or SMe_2 by other ligands, with retention of the stereochemistry of the starting products.

Neutral monodentate ligands L (L = tht, SMe_2, NCPh, PMe_3, PPh_3, CNMe) easily displace THF from *cis*-[$MR_2(THF)_2$] (ratio L:Pd = 2:1) to give the corresponding neutral mononuclear compounds *cis*-[MR_2L_2] (M = Pd, **4a**, **6a**, **11a**–**14a**; Pt, **4b**, **6b**, **11b**–**14b**). The displacement of COD from *cis*-[PdR_2(COD)] (**1a**) is more difficult, yet it works at room temperature for all the mentioned ligands except the poorly coordinating

Table 1
Arylation reactions of palladium and platinum compounds in diethyl ether using LiR

Starting material	Molar ratio starting/LiR	Product(s)	Yield (%)	Molar ratio *cis*:*trans*
[$PdCl_2$(COD)][a]	1:2	[PdR_2(COD)], **1a**	95	
[$PtCl_2$(COD)]	1:2	[PtR_2(COD)], **1b**	85	
$(NBu_4)_2[Pd_2Br_6]$	1:8.5	$(NBu_4)_2[PdR_4]$, **2a**	93	
$PtCl_2$	1:9	$(NBu_4)_2[PtR_4]$, **2b**	76	
$PtCl_2$	1:2	$(NBu_4)_2${*trans*-[$PtCl_2R_2$]}, **3b** + **2b**	70 + 7	
[$PdCl_2(tht)_2$][b]	1:2	*cis*- and *trans*-[$PdR_2(tht)_2$], **4a**, **5a**	80	1.5:1
[$PtCl_2(tht)_2$]	1:2	*cis*- and *trans*-[$PtR_2(tht)_2$], **4b**, **5b**	70	5:1
[$PdCl_2(SMe_2)_2$]	1:2	*cis*- and *trans*-[$PdR_2(SMe_2)_2$], **6a**, **7a**	80	1:2
[$PtCl_2(SMe_2)_2$]	1:2	*cis*- and *trans*-[$PtR_2(SMe_2)_2$], **6b**, **7b**	82	2.2:1

[a] COD = 1,5-cyclooctadiene.
[b] tht = tetrahydrothiophene.


MCl2(COD)
RLi
HCl
NBu4X
1/2 (NBu4)2
AgClO4, THF
OC(CD3)2/H2O
NBu4OH
Hacac
(NBu4)
2 L
2 NCPh
[PdCl2(NCPh)2]
MCl2
RLi
[PdCl2L2]
L = tht, SMe2
AgNO3
SMe2
L'
2

Scheme 1.

Table 2
Trans-arylation reactions described in this work

Starting material	Arylating reagent	Solvent	Product(s)	Yield (%)	Molar ratio *cis*:*trans* in $CDCl_3$
$PdCl_2$	$(NBu_4)_2[PdR_4]$	Refluxing acetone	$(NBu_4)_2[Pd_2(\mu\text{-}Cl)_2R_4]$, **10a**	80	
$[PdCl_2(NCPh)_2]$	*cis*-$[PdR_2(THF)_2]$	CH_2Cl_2	*cis*- and *trans*-$[Pd_2(\mu\text{-}Cl)_2R_2(NCPh)_2]$, **20a**, **21a**	82	1:2.3
$PdCl_2$	$[PdR_2(tht)_2]$	Acetone	*cis*- and *trans*-$[Pd_2(\mu\text{-}Cl)_2R_2(tht)_2]$, **22a**, **23a**	93	1:2.2
$PtCl_2$	$[PtR_2(tht)_2]$	Refluxing acetone	*cis*- and *trans*-$[Pt_2(\mu\text{-}Cl)_2R_2(tht)_2]$, **22b**, **23b**	81	1:2.7
$PdCl_2$	$[PdR_2(SMe_2)_2]$	THF	*cis*- and *trans*-$[Pd_2(\mu\text{-}Cl)_2R_2(SMe_2)_2]$, **24a**, **25a**	95	1:2.1
$[PtCl_2(tht)_2]$	$[PtR_2(tht)_2]$	Refluxing toluene	*trans*-$[PtClR(tht)_2]$, **26b**	85	
$[PtCl_2(SMe_2)_2]$	$[PtR_2(SMe_2)_2]$	Refluxing toluene	*trans*-$[PtClR(SMe_2)_2]$, **27b**	82	

NCPh. However, analogous substitutions of the diene in *cis*-$[PtR_2(COD)]$ (**1b**) had to be carried out in refluxing toluene. In addition to neutral ligands, we have investigated several reactions with the anionic ligand OH^-. The reaction of *cis*-$[MR_2(THF)_2]$ (**8a**, **8b**) with NBu_4OH(aq) in acetone leads to the formation of $(NBu_4)_2[M_2(\mu\text{-}OH)_2R_4]$ (M = Pd, **15a**; Pt, **15b**), which react with weak protic acids such as acetylacetone (Hacac) yielding mononuclear complexes $(NBu_4)[MR_2(acac)]$ (M = Pd, **16a**; Pt, **16b**). An alterna-

Table 3
Microanalytical, conductivity and selected IR data for the 3,5-dichlorotrifluorophenylpalladium derivatives

	Complex	Analysis[a]			IR/cm^{-1}		A_M^b
		%C	%H	%N	R	Ligand	
1a	*cis*-$[PdR_2(COD)]$	38.93 (39.09)	2.01 (1.97)		691, 680		
2a	$(NBu_4)_2[PdR_4]$	47.97 (48.35)	5.06 (5.22)	2.03 (2.01)	696, 687		201
4a	*cis*-$[PdR_2(tht)_2]$	35.46 (35.19)	2.54 (2.36)		693, 684		
5a	*trans*-$[PdR_2(tht)_2]$	34.84 (35.19)	2.17 (2.36)		674		
6a	*cis*-$[PdR_2(SMe_2)_2]$	30.31 (30.48)	2.04 (1.92)		696, 686		
7a	*trans*-$[PdR_2(SMe_2)_2]$	30.21 (30.48)	2.02 (1.92)		677		
8a	*cis*-$[PdR_2(THF)_2]$	36.67 (36.93)	2.54 (2.48)		707, 697		
9a	$(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$	40.58 (40.58)	4.39(4.38)	1.76 (1.69)	694, 685		202
10a	$(NBu_4)_2[Pd_2(\mu\text{-}Cl)_2R_4]$	42.92 (42.88)	4.63(4.63)	1.79 (1.79)	700, 689		180
11a	*cis*-$[PdR_2(NCPh)_2]$	44.02 (43.83)	1.73 (1.41)	3.60 (3.93)	701, 693, 683[c]	2271 ν(CN)	
12a	*cis*-$[PdR_2(PMe_3)_2]$	33.14 (32.83)	2.74 (2.76)		693, 675		
13a	*cis*-$[PdR_2(PPh_3)_2]$	55.76 (55.92)	3.05 (2.93)				
14a	*cis*-$[PdR_2(CNMe)_2]$	32.15 (32.66)	1.33 (1.03)	4.89 (4.76)	699, 691	2262, 2251 ν(CN)	
15a	$(NBu_4)_2[Pd_2(\mu\text{-}OH)_2R_4]$	44.02 (43.92)	4.89(4.87)	1.75 (1.83)	694, 688	3627 ν(OH)	126
16a	$(NBu_4)[PdR_2(acac)]$	46.42 (46.75)	4.92 (5.11)	1.54 (1.65))	701, 690		109
17a	*trans*-$[PdR_2(PMe_3)_2]$	33.24 (32.83)	2.66 (2.76)		673		
18a	*trans*-$[PdR_2(PPh_3)_2]$	55.54 (55.92)	2.89 (2.93)		670		
19a	*trans*-$[PdR_2(CNMe)_2]$	31.83 (32.66)	1.14 (1.03)	4.87 (4.76)	678	2253 ν(CN)	
20a-21a	$[Pd_2(\mu\text{-}Cl)_2R_2(NCPh)_2]$[d]	34.71 (35.09)	1.33 (1.13)	3.06 (3.15)	703, 683	2279 ν(CN)	
22a-23a	$[Pd_2(\mu\text{-}Cl)_2R_2(tht)_2]$[d]	27.76 (27.93)	1.90 (1.88)		702		
24a-25a	$[Pd_2(\mu\text{-}Cl)_2R_2(SMe_2)_2]$[d]	24.33 (23.79)	1.65 (1.50)		704	295 ν(Pd-Cl)	
26a	*trans*-$[PdRCl(tht)_2]$	32.49 (32.45)	2.98 (3.11)		695	319 ν(Pd-Cl)	
27a	*trans*-$[PdRCl(SMe_2)_2]$				699		
29a	*trans*-$[PdRCl(CNMe)_2]$	28.39 (28.33)	1.47 (1.43)	6.88 (6.61)	697	2250 ν(CN) 313 ν(Pd-Cl)	
30a	*trans*-$[PdRCl(COD)]$	37.34 (37.37)	2.75 (2.69)		699	330 ν(Pd-Cl)	

[a] Calculated values in parentheses.
[b] In acetone (5×10^{-4} M), values in Scm^2mol^{-1}.
[c] One of these signals belongs to the ligand NCPh.
[d] *cis* + *trans* mixtures. The first number refers to the *cis* isomer.

tive synthesis for **15b** consists of the treatment of $(NBu_4)_2[Pt_2(\mu\text{-}Cl)_2R_4]$ (**10b**) with 40% NBu_4OH (aq). Unlike **15b**, complex **15a** decomposes in acetone, and its isolation is only possible after a very rapid workup. The most convenient preparation of **16a** is the addition of **1a** to a methanol solution containing (NBu_4)acac.

The synthetic route to complexes containing the moiety *trans*-MR_2 is the displacement of tht or SMe_2 in *trans*-$[PdR_2(tht)_2]$ (**5a**) or *trans*-$[MR_2(SMe_2)_2]$ (**7a**, **7b**). These complexes react with stoichiometric amounts (Pd) or slight excess (Pt) of ligands L (L = PMe_3, PPh_3, CNMe) to give *trans*-$[MR_2L_2]$ (M = Pd, **17a**–**19a**; Pt, **17b**–**19b**).

2.2. Complexes with only one R group bonded to the metal center

Several *trans*-arylation reactions have been carried out and work similarly as for C_6F_5 [19]. The results are summarized in Table 2.

The mixture of *cis*- and *trans*-$[Pd_2(\mu\text{-}Cl)_2R_2(NCPh)_2]$ (**20a**, **21a**) is the most general precursor for the preparation of complexes containing the

Table 4
^{19}F NMR data at 293 K for the 3,5-dichlorotrifluorophenyl derivatives[a,b]

Complex	M = Pd		M = Pt			
	F^o	F^p	F^o	J(Pt-F^o)	F^p	J(Pt-F^p)
1	-91.16	-117.32	-93.96	337.2	-117.78	16.1
2	-85.34	-126.07	-88.58	440.4	-127.60	
3[c]			-88.06	258.5	-127.31	
4	-89.98	-118.24	-92.13	382.0	-119.04	16.1
5	-92.65	-117.16	-92.75	214.2	-117.99	11.6
6	-90.70	-118.04	-92.62	378.5	-118.87	16.4
7	-94.10	-116.98	-94.07	207.2	-117.85	11.7
8	-90.77	-118.18	-93.68	508.5	-117.78	
8aa[c,d]	-88.22	-119.98				
8ab[c,d]	-88.43 dd (6.4; 4)	-119.57				
	-88.74 dd (6.4; 4)	-119.45				
8ac[c,d]	-89.05	-119.10				
8ba[c]			-91.20	512.2	-122.13	16.5
8bb[c]			-91.25 t (4.6)	510.3	-121.50	16.5
			-91.82 t (4.6)	504.1	-121.39	15.6
8bc[c]			-92.02	501.3	-120.76	16.3
9	-87.97	-121.68	-90.48	475.9	-123.15	
10	-88.43	-121.61	-91.87	485.6	-122.81	
11	-90.59	-118.98	-93.66	440.9	-119.60	11.5
12	-90.07 m	-119.31 m	-91.93 m	316.4	-119.75 m	13.7
13	-90.05 m[e]	-120.72 m	-91.71 m	301.0	-121.24 m	13.2
14	-90.02	-119.01	-92.11	356.6	-118.97	14.4
15[c]	-86.49	-123.63	-91.54	494.7	-125.78	
16	-89.21	-122.07	-90.80	488.7	-124.41	
17	-91.25 t [5]	-118.47 t [2.5]	-92.31	294.0	-119.52 t [2.4]	14.1
18	-88.10 t [4.8]	-120.83 t [2]	-88.86	227.4	-121.94 t [2]	
20	-95.33	-116.30				
21	-95.33	-116.60				
22	-94.26	-116.11	-94.15	298.6	-117.23	
23	-94.48	-116.27	-94.29	304.7	-117.48	
24	-94.82	-115.99				
25	-94.99	-116.11				
26	-93.03	-116.05	-93.15	307.7	-117.80	17.9
27	-94.47	-116.06	-94.51	306.2	-117.85	18.0
28			-93.33	286.6	-118.07	12.1
29	-89.98	-116.63	-90.80	357.5	-117.95	16.6
30	-95.21	-116.30	-96.26	257.6	-116.92	15.2

[a] $CDCl_3$, unless otherwise indicated; J(F-F)/Hz values are in parentheses and J(P-F)/Hz in square brackets.
[b] All the signals were singlets unless otherwise indicated.
[c] $(CD_3)_2CO$.
[d] 190 K.
[e] Apparent triplet.^{19}F NMR data at 293 K for the 3,5-dichlorotrifluorophenyl derivates[a,b]

moiety 'PdClR'. Thus, on reaction with neutral ligands L_2 (L_2 = 2 tht, 2 CNMe, COD) the mixture **20a**–**21a** is converted into $[PdClRL_2]$ (**26a**, **29a**, **30a**) in high yield. The chloro-bridged complexes *cis*- and *trans*-$[Pd_2(\mu\text{-}Cl)_2R_2L_2]$ (L = tht, **22a**, **23a**; SMe_2, **24a**, **25a**) can be used also as precursors, but because of the better coordination ability of tht or SMe_2 towards Pd or Pt compared to PhCN, they are not as versatile as **20a**–**21a**.

The mixture of *cis*- and *trans*-$[Pt_2(\mu\text{-}Cl)_2R_2(tht)_2]$ (**22b**, **23b**) reacts with tht giving *trans*-$[PtClR(tht)_2]$ (**26b**), whereas reaction with CNMe generates a mixture of *cis*- and *trans*-$[PtClR(CNMe)_2]$ (**28b**, **29b**). On the other hand, reaction of the mixture **22b**–**23b** with the less coordinating COD affords *cis*-[PtClR(COD)] (**30b**) and **26b**.

Attempts to prepare complexes $[PtClRL_2]$ by arylation of $[PtCl_2L_2]$ by LiR (molar ratio 1:1) were unsuccessful leading to mixtures of $[PtR_2L_2]$ and the starting material. However, equimolar amounts of $[PtR_2L_2]$ and $[PtCl_2L_2]$ (L = tht, SMe_2) in refluxing toluene give *trans*-$[PtClRL_2]$ (**26b**, **27b**) in very good yield.

3. Characterization of the complexes and discussion

Elemental analyses, IR spectral data and conductivities are listed in Tables 3 and 4, ^{19}F NMR data are summarized in Table 5, and ^{1}H and $^{31}P\{^{1}H\}$ in Table 6.

The solid-state IR spectra for all the isolated complexes exhibit characteristic absorptions for the R group in the following regions: 1590–1560, 1450–1350, 1050–1040, 800–750 and 710–670 cm^{-1}. As reported for other polyfluorophenyl groups [2,5], one of the absorption regions (710–670 cm^{-1}) associated to the R–M fragment can be structurally informative. In effect, the *cis* isomers exhibit two strong bands in this range, whereas the *trans* isomers show only one.

The ^{19}F NMR spectra of the complexes with 3,5-$C_6Cl_2F_3$ groups (Table 5) are simple compared to those of the other polyfluorophenyl groups, and this greatly facilitates their characterization and the study of their behavior in solution. For instance, the C_6F_5 group constitutes a five-spin system involving three or five (when the two halves of the ring become inequivalent)

Table 5
^{1}H and ^{31}P NMR data at 293 K for the dichlorotrifluorophenyl derivatives[a]

Complex	M = Pd		M = Pt	
	^{1}H NMR	^{31}P NMR	^{1}H NMR	^{31}P NMR
1	COD: 5.78 (m, br, 4 H, CH), 2.74 (m, 8 H, CH_2)		COD: 5.34 (m, 4 H, CH) $J_{Pt\text{-}H}$ = 45.2; 2.59 (m, 8 H, CH_2)	
4	tht: 2.88 (m, 8 H), 1.87 (m, 8 H)		tht: 3.02 (m, 8 H) $J_{Pt\text{-}H}$ = 33.2; 1.86 (m, 8 H)	
5	tht: 2.68 (m, 8 H), 1.85 (m, 8 H)		tht: 2.77 (m, br, 8 H) $J_{Pt\text{-}H}$ = 61.9; 1.83, (m, br, 8 H)	
6	SMe_2: 2.15 (s, 12 H)		SMe_2: 2.30 (s, 12 H) $J_{Pt\text{-}H}$ = 33.1	
7	SMe_2: 2.08 (s, 12 H)		SMe_2: 2.20 (s, 12 H) $J_{Pt\text{-}H}$ = 60	
8	THF: 3.78 (m, 4 H) 1.82 (m, 4 H)		THF: 3.93 (m, 4 H), 1.87 (m, 4 H)	
11	NCPh: 7.75-7.65 (m, 6 H), 7.57-7.48 (m, 4 H)		NCPh: 7.77-7.70 (m, 6 H), 7.57-7.50 (m, 4 H)	
12	PMe_3: 1.30 (m, 18 H) [N = 8.5][b]	-18.9 m	PMe_3: 1.43 (m, 18 H) [N = 9.2][b] $J_{Pt\text{-}H}$ = 26.3	-26.8 m $J_{Pt\text{-}P}$ = 2276
13	PPh_3: 7.40-7.10 (m, 30 H)	19.1 m	PPh_3: 7.41-7.05 (m, 30 H)	12.2 m $J_{Pt\text{-}P}$ = 2376
14	CNMe: 3.39 (s, 6 H)		CNMe: 3.40 (s, 6 H) $J_{Pt\text{-}H}$ = 13.2	
15[c]	μ-OH: -2.89 (s, 2 H)		μ-OH: -0.97 (s, 2 H)	
16	acac: 5.24 (s, 1 H), 1.84 (s, 6 H, Me)		acac: 5.29 (s, 1 H), 1.64 (s, 6 H, Me)	
17	PMe_3: 1.07 (m, 18 H) [N = 7][b]	-13.4 m	PMe_3: 1.16 (m, 18 H) [N = 7.3][b] $J_{Pt\text{-}H}$ = 31	-19.1 $J_{Pt\text{-}P}$ = 2484
18	PPh_3: 7.50-7.20 (m, 30 H)	2.5 m	PPh_3: 7.50-7.15 (m, 30 H)	14.8 $J_{Pt\text{-}P}$ = 2785
20-21	NCPh: 7.71-7.48 (m, 10 H)			
22-23	tht: 3.30-2.60 (br, 8 H), 2.20-1.90 (br, 8 H)		tht: 3.19 (m, 4 H), 2.83 (m, 4 H), 2.23 (m, 4 H), 1.93 (m, 4 H)	
24-25	SMe_2: 2.32 (s, 12 H)			
26	tht: 3.04 (br, 8 H), 2.02 (m, 8 H)		tht: 3.37 (br, 4 H), 2.87 (br, 4 H), 1.85-2.25 (br, 8 H)	
27	SMe_2: 2.35 (s, 12 H)		SMe_2: 2.46 (s, 12 H) $J_{Pt\text{-}H}$ = 52	
28			CNMe: 3.40 (s, 3 H) $J_{Pt\text{-}H}$ = 19.3; 3.50 (s, 3 H) $J_{Pt\text{-}H}$ = 11.9	
29	CNMe: 3.40 (s, 6H)		CNMe: 3.45 (s, 6 H) $J_{Pt\text{-}H}$ = 14.5	
30	COD: 6.23 (m, 2 H, CH), 5.60 (m, 2 H, CH), 2.87-2.60 (m, 8 H, CH_2) 2.42 (m, 4 H, CH_2)		COD: 5.90 (m, 2 H, CH) $J_{Pt\text{-}H}$ = 41.9; 4.92 (m, 2 H, CH) $J_{Pt\text{-}H}$ = 469.6; 2.67 (m, 4 H, CH_2);	

[a] $CDCl_3$, unless otherwise indicated; J(P-H)/Hz values are in square brackets. Additional peaks from $(NBu_4)^+$, with the correct intensities, are found in the spectra of the ionic complexes.
[b] $X_9AA'X'_9$ spin system, N = J(A-X) + J(A-X'). [c] $(CD_3)_2CO$.

Table 6
^{1}H and ^{31}P NMR data at 293 K for the dichlorotrifluorophenyl derivatives[a]

Complex	M = Pd		M = Pt	
	^{1}H NMR	^{31}P NMR	^{1}H NMR	^{31}P NMR
1	COD: 5.78 (m, br, 4 H, CH), 2.74 (m, 8 H, CH_2)		COD: 5.34 (m, 4 H, CH) $J_{Pt-H} = 45.2$; 2.59 (m, 8 H, CH_2)	
4	tht: 2.88 (m, 8 H), 1.87 (m, 8 H)		tht: 3.02 (m, 8 H) $J_{Pt-H} = 33.2$; 1.86 (m, 8 H)	
5	tht: 2.68 (m, 8 H), 1.85 (m, 8 H)		tht: 2.77 (m, br, 8 H) $J_{Pt-H} = 61.9$; 1.83 (m, br, 8 H),	
6	SMe_2: 2.15 (s, 12 H)		SMe_2: 2.30 (s, 12 H) $J_{Pt-H} = 33.1$	
7	SMe_2: 2.08 (s, 12 H)		SMe_2: 2.20 (s, 12 H) $J_{Pt-H} = 60$	
8	THF: 3.78 (m, 4 H), 1.82 (m, 4 H)		THF: 3.93 (m, 4 H), 1.87 (m, 4 H)	
11	NCPh: 7.75–7.65 (m, 6 H), 7.57–7.48 (m, 4 H)		NCPh: 7.77–7.70 (m, 6 H), 7.57–7.50 (m, 4 H)	
12	PMe_3: 1.30 (m, 18 H) [$N = 8.5$][b]	−18.9 m	PMe_3: 1.43 (m, 18 H) [$N = 9.2$][b] $J_{Pt-H} = 26.3$	−26.8 m $J_{Pt-P} = 2276$
13	PPh_3: 7.40–7.10 (m, 30 H)	19.1 m	PPh_3: 7.41–7.05 (m, 30 H)	12.2 m $J_{Pt-P} = 2376$
14	CNMe: 3.39 (s, 6 H)		CNMe: 3.40 (s, 6 H) $J_{Pt-H} = 13.2$	
15[c]	μ-OH: −2.89 (s, 2 H)		μ-OH: −0.97 (s, 2 H)	
16	acac: 5.24 (s, 1 H), 1.84 (s, 6 H, Me)		acac: 5.29 (s, 1 H), 1.64 (s, 6 H, Me)	
17	PMe_3: 1.07 (m, 18 H) [$N = 7$][b]	−13.4 m	PMe_3: 1.16 (m, 18 H) [$N = 7.3$][b] $J_{Pt-H} = 31$	−19.1 $J_{Pt-P} = 2484$
18	PPh_3: 7.50−7.20 (m, 30 H)	2.5 m	PPh_3: 7.50–7.15 (m, 30 H)	14.8 $J_{Pt-P} = 2785$
20–21	NCPh: 7.71–7.48 (m, 10 H)			
22–23	tht: 3.30–2.60 (br, 8 H), 2.20–1.90 (br, 8 H)		tht: 3.19 (m, 4 H), 2.83 (m, 4 H), 2.23 (m, 4 H), 1.93 (m, 4 H)	
24–25	SMe_2: 2.32 (s, 12 H)			
26	tht: 3.04 (br, 8 H), 2.02 (m, 8 H)		tht: 3.37 (br, 4 H), 2.87 (br, 4 H), 1.85–2.25 (br, 8 H)	
27	SMe_2: 2.35 (s, 12 H)		SMe_2: 2.46 (s, 12 H) $J_{Pt-H} = 52$	
28			CNMe: 3.40 (s, 3 H) $J_{Pt-H} = 19.3$; 3.50 (s, 3 H) $J_{Pt-H} = 11.9$	
29	CNMe: 3.40 (s, 6H)		CNMe: 3.45 (s, 6 H) $J_{Pt-H} = 14.5$	
30	COD: 6.23 (m, 2 H, CH), 5.60 (m, 2 H, CH), 2.87–2.60 (m, 8 H, CH_2)		COD: 5.90 (m, 2 H, CH) $J_{Pt-H} = 41.9$; 4.92 (m, 2 H, CH) $J_{Pt-H} = 469.6$; 2.67 (m, 4 H, CH_2); 2.42 (m, 4 H, CH_2)	

[a] $CDCl_3$, unless otherwise indicated; J(P–H)/Hz values are in square brackets. Additional peaks from $(NBu_4)^+$, with the correct intensities, are found in the spectra of the ionic complexes.
[b] $X_9 AA' X_9'$ spin system, $N = J(A - X) + J(A - X')$.
[c] $(CD_3)_2CO$.

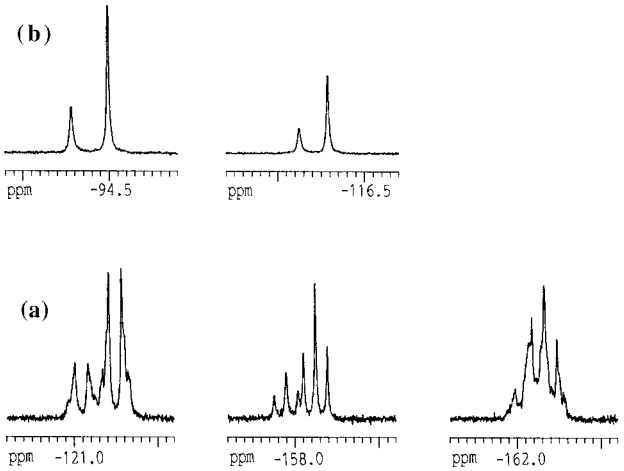


Fig. 1. ^{19}F NMR ($CDCl_3$, 282.35 MHz) spectra of *cis*- and *trans*-[$Pd_2(\mu$-Cl)$_2R_2$(tht)$_2$] for R = C_6F_5 (**a**) and 3,5-$C_6Cl_2F_3$ (**b**), recorded using the same conditions (on 8 mM solutions, 8 pulses). The predominant species are the *trans* isomers.

different chemical shifts and having very significant $^3J(F^o–F^m)$ and $^3J(F^m–F^p)$ coupling constants (about 20 Hz) between mutually *ortho* fluorine atoms [20]. This gives rise to multiplet signals, can produce often overlapping of close signals, and complicates noticeably the simulation of the spectra. On the contrary, the complexes with 3,5-$C_6Cl_2F_3$ have only mutually *meta* fluorine atoms with very small $^4J(F^o–F^p)$ (usually $<$ 0.5 Hz). This small coupling can be suppressed by reducing the digital resolution below this limit (which is usually the case), whereupon all the signals become singlets, unless other couplings are involved. Thus, when the two halves of the aryl ring are equivalent they display two sharp singlets of relative intensities 2:1. If the two halves of the ring are inequivalent, three signals with 1:1:1 intensities are observed. This simplification of the spectral features can be seen in the examples discussed below.

Fig. 1 shows the ^{19}F NMR spectra of the complexes [$Pd_2(\mu$-Cl)$_2R_2$(tht)$_2$] for R = C_6F_5 (a) and 3,5-$C_6Cl_2F_3$ (b) recorded under similar conditions. These neutral binuclear double-bridged complexes (also the Pt complex, see Table 2) turn out to be mixtures of the *cis*- and *trans* isomers in $CDCl_3$ solutions. The advantages of using 3,5-$C_6Cl_2F_3$ are obvious: Because their signals are singlets, the signal-to-noise ratio is much better, and their resonances do not overlap. Even when ^{19}F is a nucleus with high receptivity, an improvement in the signal-to-noise ratio can save much time when kinetic experiments are undertaken. Moreover, the simplicity of the signals makes line–shape analysis, when needed, much easier than for C_6F_5 systems [21]. Addition of benzene to these $CDCl_3$ solutions produces, in all cases, an increase of the more intense resonance; therefore, we conclude that the complexes undergo exchange within

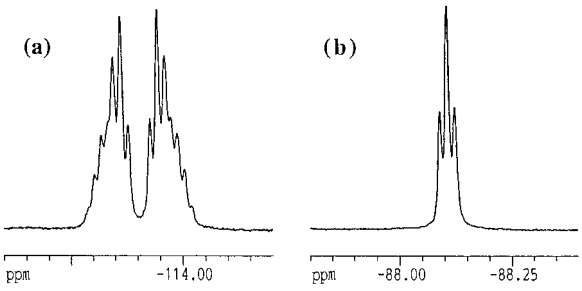


Fig. 2. 3^{19}F NMR signals of the F^o atoms of *trans*[$PdR_2(PPh_3)_2$] for R = C_6F_5 (**a**) and 3,5-$C_6Cl_2F_3$ (**b**).

seconds, and the predominant species are the *trans* isomers that should be favored in less polar solvents [22]. Addition of acetone to a mixture of *cis*- and *trans*-[$Pt_2(\mu$-Cl)$_2R_2$(tht)$_2$] (**22b**, **23b**) in $CDCl_3$ produces the contrary effect, whereas for the palladium complexes, we observe that the signals become broader probably due to an increase in the exchange rate.

Fig. 2 shows the F^o resonances for the complexes *trans*-[$PdR_2(PPh_3)_2$] for R = C_6F_5 (a) and 3,5-$C_6Cl_2F_3$ (b). Where the signal is not clear for R = C_6F_5, due to the existence of large $F^o–F^m$ couplings, a characteristic triplet can be easily seen for R = 3,5-$C_6Cl_2F_3$.

A third simple illustration is given by the spectra of the complexes *cis*-[$MR_2(THF)_2$] (M = Pd, **8a**; Pt, **8b**). The THF ligand is very labile and can readily be displaced even by weak ligands. In fact, the $(CD_3)_2CO$ solutions of the platinum complex **8b** (Fig. 3) show four F^o signals and four F^p signals in the ^{19}F NMR spectrum at 293 K, plus the corresponding Pt satellites. The signals are assigned to the following products: *cis*-

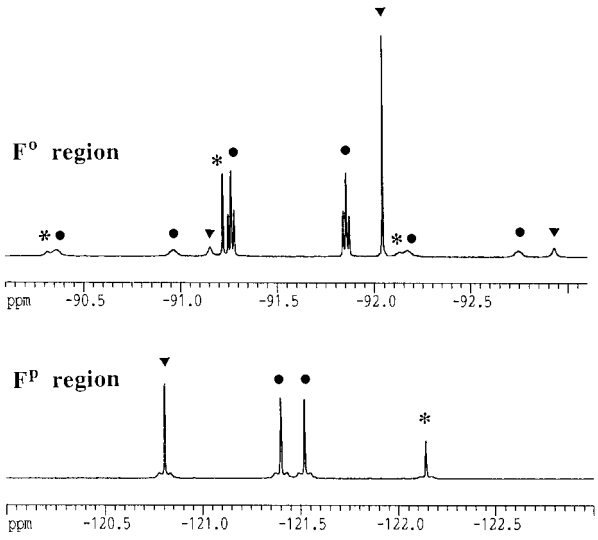


Fig. 3. ^{19}F NMR spectrum of a solution of *cis*-[$PtR_2(THF)_2$] (**8b**, R = 3,5-$C_6Cl_2F_3$) in wet $(CD_3)_2CO$. Signals of *cis*-[$PtR_2(H_2O)_2$] (**8ba**, $*$) *cis*-[$PtR_2(H_2O)(CO(CD_3)_2)$] (**8bb**, •), and *cis*-[$PtR_2(CO(CD_3)_2)_2$] (**8bc**, ▼) are observed (see text and Scheme 1).

$[PtR_2(H_2O)_2]$ (**8ba**), *cis*-$[PtR_2(H_2O)(CO(CD_3)_2)]$ (**8bb**), and *cis*-$[PtR_2(CO(CD_3)_2)_2]$ (**8bc**). Their proportions depend on the H_2O contents in the deuterated solvent, the amount of **8ba** and **8bb** increasing upon addition of H_2O to the solvent. The coordinated H_2O resonances are localized in the ^1H NMR spectrum at 6.65 and 6.78 ppm for **8ba** and **8bb**, respectively.

An interesting feature is that the F^o resonances of the two inequivalent R groups in **8bb** appear as triplets rather than as singlets. This reveals the existence of F–F coupling between the rings. Moreover, the triplet appearance indicates that each F^o in one ring couples equally to the two $F^{o'}$ of the other ring. This is only possible if the rotation of the ring around the C–Pt bond is fast, converting the *syn*- and *anti* positions relative to the coordination plane. This kind of feature is impossible to observe in the corresponding C_6F_5 derivatives due to the inherent complexity of the signals. The ^{195}Pt coupling constants are in the order of values reported for *cis*-$Pt(C_6F_5)_2$ moieties [21,23–25], and suggest that the *trans* influence of H_2O is slightly smaller than that of $(CD_3)_2CO$.

In the case of the palladium analog **8a**, two broad singlets were obtained in the ^{19}F NMR spectrum in $(CD_3)_2CO$ at 293 K, but they were resolved when the temperature was lowered, to show those expected for the presence of *cis*-$[PdR_2(H_2O)_2]$ (**8aa**), *cis*-$[PdR_2(H_2O)(CO(CD_3)_2)]$ (**8ab**), and *cis*-$[PdR_2(CO(CD_3)_2)_2]$ (**8ac**). At 190 K, the *ortho* fluorine signals due to **8ab** show a characteristic splitting pattern of doublet of doublets (6.4 and 4 Hz), because the rotation of the aryl group is slow at this temperature. The H_2O resonances are localized at this temperature in the ^1H NMR spectrum at 6.30 and 6.40 ppm for **8aa** and **8ab**, respectively. The fact that the exchange **8aa** ⇌ **8ab** ⇌ **8ac** is fast whereas the exchange **8ba** ⇌ **8bb** ⇌ **8bc** is too slow to be detected suggests that they operate by associative mechanisms, fast for Pd but slow for Pt.

4. Conclusions

The general precursors described in this paper allow to prepare almost any isomer of any complex containing one or two aryl rings 3,5-$C_6Cl_2F_3$, both for Pd and for Pt. The sensitivity and simplicity of their ^{19}F spectra make these complexes spectroscopically more convenient than the corresponding C_6F_5 complexes used so far. In addition, some features hidden by the complexity of the spectra in C_6F_5 derivatives, can be seen in the new 3,5-$C_6Cl_2F_3$ complexes, such as inter-ring F–F couplings. Other advantages of the use of these 3,5-$C_6Cl_2F_3$ complexes, particularly for mechanistic studies, will be shown in forthcoming papers.

5. Experimental

All reactions involving LiR or PMe_3 were performed under nitrogen atmosphere, although subsequent manipulations were carried out in air, except where otherwise stated. Solvents were dried and purified according to standard procedures [26]. 1,3,5-$C_6Cl_3F_3$ was purchased from Fluorochem and used as received. Methyl isocyanide was prepared as described elsewhere [27]. All other reagents were obtained from commercial sources and used without further purification. The complexes $[MCl_2(COD)]$, $(NBu_4)_2[Pd_2Br_6]$, $[MCl_2(tht)_2]$ and $[MCl_2(SMe)_2]$ were prepared by reported methods [15,28–32].

C, H and N analyses were carried out on a Perkin-Elmer 2400B microanalyzer. IR spectra were recorded (in the range 4000–200 cm^{-1}) on a Perkin-Elmer 883 spectrophotometer using samples mulled in Nujol between polyethylene films. Conductivities were measured with a Crison 522 conductimeter. Conductivity data were obtained at sample concentrations ca. 5×10^{-4} M in acetone solutions at room temperature. ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC300 or ARX300 instruments (at 300.13, 282.35, and 121.44 MHz, respectively) at room temperature unless otherwise stated. Chemical shifts are relative to TMS (^1H NMR), $CFCl_3$ at 293 K (^{19}F NMR), or external 85% H_3PO_4 (^{31}P NMR), with downfield values reported as positive.

5.1. Arylation reactions of palladium and platinum compounds

5.1.1. Preparation of $[MR_2(COD)]$ (**1a**, **1b**)

n-Buthyllithium (5 ml of 1.6 M solution in hexane, 8 mmol) was added dropwise to a solution of 1,3,5-$C_6Cl_3F_3$ (1.88 g, 8 mmol) in dry Et_2O (30 ml), at −78°C, under N_2 atmosphere. After the reaction mixture was stirred at this temperature for 30 min. $[PdCl_2(COD)]$ (1.14 g, 4 mmol) was added, and the suspension was allowed to warm to room temperature in 6 h. Moist Et_2O (10 ml) was added and the suspension evaporated to dryness. The residue was extracted with CH_2Cl_2 (3×80 ml) and the resulting filtrates were combined and evaporated to dryness. Addition of isopropanol (15 ml) to the residue and filtration gave a white solid, which was washed with isopropanol and air-dried (**1a**, 95%). **1b** was prepared similarly (85%).

5.1.2. Preparation of $(NBu_4)_2[PdR_4]$ (**2a**)

To a solution of LiR (10 mmol) in Et_2O (50 ml), at −78°C, under a N_2 atmosphere, was added $(NBu_4)_2[Pd_2Br_6]$ (1.387 g, 1.18 mmol). The reaction mixture was allowed to warm to room temperature, and stirred overnight. Moist Et_2O (10 ml) was added and the suspension evaporated to dryness. The residue was extracted with acetone (80 ml), NBu_4Br (0.838 g, 2.6 mmol) was then added, and the resulting solution was

evaporated to dryness. Addition of ethanol (25 ml) to the residue and filtration gave a white solid, which was washed with ethanol, and air-dried (**2a**, 93%).

*5.1.3. Preparation of $(NBu_4)_2[PtR_4]$ (**2b**) and $(NBu_4)_2\{trans\text{-}[PtCl_2r_2]\}$*

To a solution of LiR (9 mmol) in Et_2O (50 ml) at −78°C, under N_2, was added $PtCl_2$ (0.266 g, 1 mmol). The reaction mixture was allowed to warm to room temperature and stirred overnight. Et_2O (10 ml), moistened with some drops of water, was added and the solution was evaporated. The residue was treated with acetone (50 ml), filtered and the resulting solution evaporated to dryness. The solid obtained was extracted with ethanol (20 ml), and NBu_4Br (0.645 g, 2 mmol) was added to the filtrate to give a white solid, which was filtered, washed with ethanol, and air-dried (**2b**, 76%). A similar procedure starting from LiR (11.28 mmol), $PtCl_2$ (1.5 g, 5.64 mmol), and NBu_4Br (3.63 g, 11.28 mmol) gave a mixture of yellow **3b** and **2b** (10:1 proportion). The separation of **3b** (65%) from the mixture was achieved by recrystallization in acetone.

*5.1.4. Preparation of $[MR_2L_2]$ (L = tht, SMe_2) (**4-7**)*

To a solution of LiR (8.48 mmol) in Et_2O (50 ml) at −78°C, under N_2, was added $[PdCl_2(tht)_2]$ (1.5 g, 4.24 mmol), and the mixture was allowed to warm to room temperature and stirred for 4 h. The resulting suspension was hydrolized with moist Et_2O (10 ml), and evaporated to dryness. The residue was extracted with CH_2Cl_2 (100 ml), and the filtrate was evaporated to 5 ml, treated with ethanol (5 ml), and concentrated to 5 ml. The resulting suspension was filtered and the solid washed with cold ethanol and air-dried (mixture of **4a** and **5a**, 80%). The solid mixture was first extracted with CH_2Cl_2 (2 × 30 ml) yielding a residue of pure *trans* isomer **5a**. The organic solution, which still contained *cis*- and *trans* complexes, was evaporated to dryness and the solid was chromatographied (silica gel 60, CH_2Cl_2:*n*-hexane 1:5) giving pure fractions of **4a** and **5a**.

A mixture of *cis*- and *trans*-$[PdR_2(SMe_2)_2]$ (**6a**, **7a**), and the analogous Pt complexes (**4b**–**7b**) were prepared similarly (see Table 1). Pure **7a** can be separated from the mixture of isomers by extraction in Et_2O.

5.2. Complexes with two R groups bonded to the metal center

*5.2.1. Preparation of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2R_4]$ (**9a**)*

To a solution of $[PdR_2(COD)]$ (0.8 g, 1.3 mmol) in acetone (40 ml), was added NBu_4Br (0.52 g, 1.6 mmol). After 10 min the solvent was evaporated, and the residue was stirred with isopropanol (10 ml) to give a pale yellow solid (**9a**, 96%).

*5.2.2. Preparation of $(NBu_4)_2[Pt_2(\mu\text{-}I)_2R_4]$ (**9b**)*

A mixture of $[PtR_2(COD)]$ (1.5 g, 2.13 mmol) and NBu_4I (0.788 g, 2.13 mmol) was refluxed in toluene (60 ml) for 4 h. The resulting colorless solution was evaporated to dryness and the residue washed with pentane (2 × 30 ml) to remove the free COD. After a new addition of toluene (60 ml), the mixture was refluxed for 3 h and concentrated in vacuo to dryness. Addition of isopropanol to the resulting residue gave a white solid, which was filtered, washed with isopropanol, and dried (**9b**, 88%).

*5.2.3. Preparation of $(NBu_4)_2[M_2(\mu\text{-}Cl)_2R_4]$ (**10a**, **10b**)*

To a solution of $(NBu_4)_2[PtR_4]$ (1.48 g, 1 mmol) in a methanol/acetone (30:30, 50 ml) mixture was added dropwise a solution of HCl (4.5 ml, 2 mmol) in methanol. The solution was stirred for 90 min at room temperature, then concentrated to 5 ml. The white precipitate was filtered, and washed with methanol (**10b**, 94%). **10a** was prepared similarly (90%). An alternative and more convenient synthesis of **10a** is to reflux $(NBu_4)_2[PdR_4]$ (1.39 g, 1 mmol) and $PdCl_2$ (0.178 g, 1 mmol) in acetone for 8 h.

*5.2.4. Preparation of $[MR_2(THF)_2]$ (**8a**, **8b**)*

To a solution of $(NBu_4)_2[M_2(\mu\text{-}X)_2R_4]$ (0.7 mmol) in dry THF (25 ml) under N_2 was added $AgClO_4$ (0.29 g, 1.4 mmol). After 12 h stirring the precipitate (AgX) was filtered off and the solution evaporated to dryness. The residue was extracted with dry Et_2O (2 × 70 ml) under N_2, and the insoluble NBu_4ClO_4 was removed. The clear solution was vacuum-concentrated to ca. 5 ml. Upon addition of pentane (10 ml), a white precipitate appeared (**8a**, 84%; **8b**, 77%).

*5.2.5. Preparation of trans-$[PtR_2(SMe_2)_2]$ (**7b**)*

A mixture of $(NBu_4)_2[PtCl_2R_2]$ (0.450 g, 0.39 mmol) and $AgNO_3$ (0.133 g, 0.78 mmol) in acetonitrile (40 ml) was stirred for 10 min, and then SMe_2 (1 ml, 13.6 mmol) was added. After 2 h stirring, the AgCl was filtered off, and the solution evaporated to dryness. Addition of methanol (10 ml) to the residue gave a white solid that was recrystallized from CH_2Cl_2–methanol (**7b**, 65%).

*5.2.6. Preparation of cis-$[MR_2L_2]$ (**11-14**)*

To a solution of *cis*-$[MR_2(THF)_2]$ (0.15 mmol) in CH_2Cl_2 (30 ml) was added L (0.30 mmol), and the mixture was stirred for 15 min. The resulting colorless solution was evaporated to dryness to give white *cis*-$[MR_2L_2]$, which was washed with *n*-pentane and air-dried (quantitative yields). An alternative and more convenient synthesis of *cis*-$[PdR_2L_2]$ (**12a**–**14a**) is achieved starting from *cis*-$[PdR_2(COD)]$ (0.092 g, 0.15 mmol) and L (0.30 mmol), with similar work up.

*5.2.7. Preparation of $(NBu_4)_2[M_2(\mu\text{-}OH)_2R_4]$ (**15a**, **15b**)*

A 40% aqueous solution of NBu_4OH (131 μl, 0.20 mmol) was added to an acetone (10 ml) solution of *cis*-$[MR_2(THF)_2]$ (0.20 mmol). The mixture was stirred for 5 min and concentrated in vacuo to 2 ml. Addition of water (5 ml) caused precipitation of a white solid, which was collected by filtration, washed with water and air-dried (**15a**, 85%; **15b**, 91%). An alternative synthesis of **15b** is to start from $(NBu_4)_2[Pt_2(\mu\text{-}Cl)_2R_4]$ (0.8 g, 0.46 mmol) and a 1.2 N aqueous solution of NBu_4OH (1.15 ml, 1.4 mmol), with 30 min stirring and similar work up (97%).

*5.2.8. Preparation of $(NBu_4)[PdR_2(acac)]$ (**16a**)*

A 40% aqueous solution of NBu_4OH (160 μl, 0.244 mmol) was added to a methanol (30 ml) solution of Hacac (25 μl, 0.244 mmol), and the mixture was stirred for 15 min before adding *cis*-$[PdR_2(COD)]$ (0.15 g, 0.244 mmol). The suspension formed was stirred for 4 h and concentrated in vacuo to 5 ml giving a white solid, which was removed by filtration, washed with methanol (5 ml) and air-dried (**16a**, 90%).

*5.2.9. Preparation of $(NBu_4)[PtR_2(acac)]$ (**16b**)*

A mixture of $(NBu_4)_2[Pt_2(\mu\text{-}OH)_2R_4]$ (0.125 g, 0.073 mmol) and Hacac (15 μl, 0.146 mmol) was refluxed in acetone (30 ml) for 6 h. The resulting colorless solution was evaporated to dryness, and the residue washed with methanol (5 ml) and dried (**16b**, 80%).

*5.2.10. Preparation of trans-$[MR_2L_2]$ (**17-19**)*

To a solution of *trans*-$[MR_2(SMe_2)_2]$ (0.12 mmol) in CH_2Cl_2 (30 ml) was added L (0.25 mmol), and the mixture was stirred for 2 h. The resulting solution (or suspension) was evaporated to dryness to give white *trans*-$[MR_2L_2]$, which was washed with *n*-pentane or Et_2O and air-dried (quantitative yields). *trans*-$[PdR_2(tht)_2]$ can also be used as starting material.

For ligands of donor ability similar to SMe_2, excess must be used. Thus, a mixture of *trans*-$[PtR_2(SMe_2)_2]$ (0.108 g, 0.15 mmol) and tht (53 μl, 0.6 mmol) was refluxed in toluene (30 ml) for 6 h. The resulting colorless solution was evaporated to dryness, and the residue washed with methanol (5 ml) and dried (**5b**, 88%).

5.3. Complexes with only one R group bonded to the metal center

*5.3.1. Preparation of cis- and trans-$[Pd_2(\mu\text{-}Cl)_2R_2(NCPh)_2]$ (**20a-21a**)*

A mixture of *cis*-$[PdR_2(THF)_2]$ (1 g, 1.54 mmol) and $[PdCl_2(NCPh)_2]$ (0.59 g, 1.54 mmol) was stirred in CH_2Cl_2 (30 ml) for 30 min. The resulting solution was evaporated to dryness and the oily residue was triturated with pentane (10 ml) to give a yellow-brown solid, which was filtered and air-dried (**20a**–**21a**, 82%).

*5.3.2. Preparation of cis- and trans-$[M_2(\mu\text{-}Cl)_2R_2L_2]$ (**22-25**)*

A mixture of $[PdR_2(tht)_2]$ (0.85 g, 1.245 mmol), $PdCl_2$ (0.22 g, 1.245 mmol), and acetone (75 ml) was stirred overnight. The resulting suspension was evaporated to dryness, giving a yellow solid which was washed with Et_2O, filtered and air-dried (**22a**–**23a**, 93%). *cis*- and *trans*-$[Pd_2(\mu\text{-}Cl)_2R_2(SMe_2)_2]$ was prepared in the same way using THF as solvent (**24a**–**25a**, 95%). The platinum analogue to **22a**–**23a** was prepared in refluxing acetone with similar work up (**22b**–**23b**, 81%).

*5.3.3. Preparation of trans-$[MClRL_2]$ (L = tht, **26**; SMe_2, **27**)*

To a suspension of $[M_2(\mu\text{-}Cl)_2R_2(tht)_2]$ (0.15 mmol) in $CHCl_3$ (30 ml) was added an excess of tht (37 μl, 0.42 mmol). The resulting solution was stirred for 30 min and evaporated to dryness. The residue was triturated with *n*-pentane, filtered and air-dried (**26a**, 85%; **26b**, 88%). Using the same procedure, it was not possible to prepare pure *trans*-$[PdClR(SMe_2)_2]$ (**27a**) because a small amount of $[Pd_2(\mu\text{-}Cl)_2R_2(SMe_2)_2]$ was always present (they are in equilibrium).

Alternatively, a mixture of $[PtR_2L_2]$ (0.15 mmol) and $[PtCl_2L_2]$ (0.15 mmol) was refluxed in toluene (30 ml) for 8 h. The resulting colourless solution was evaporated to dryness, and the residue washed with *n*-pentane (15 ml) and dried (**26b**, 85%; **27b**, 82%).

*5.3.4. Preparation of $[PdClRL_2]$ (L_2 = 2CNMe, **29a**; COD, **30a**)*

To a solution of $[Pd_2(\mu\text{-}Cl)_2R_2(NCPh)_2]$ (0.210 g, 0.236 mmol) in $CHCl_3$ (30 ml) was added L_2 (0.50 mmol). The resulting solution was stirred for 30 min and evaporated to dryness. The residue was triturated with methanol (10 ml), filtered and air-dried (**29a**, 88%; **30a**, 85%).

*5.3.5. Preparation of cis- and trans-$[PtClR(CNMe)_2]$ (**28b**, **29b**)*

To a yellow suspension of $[Pt_2(\mu\text{-}Cl)_2R_2(tht)_2]$ (0.15 g, 0.145 mmol) in $CHCl_3$ (30 ml) was added CNMe (0.5 mmol), and the mixture was stirred for 1 h. The resulting colourless solution was evaporated to dryness and the residue was triturated with Et_2O (20 ml), filtered, washed with Et_2O (2×10 ml), and air-dried (**28b**, 60%). The Et_2O solution was evaporated to dryness and the residue stirred with *n*-pentane giving a solid that was identified as a mixture of **29b** and a small amount of **28b**.

*5.3.6. Preparation of cis-[PtClR(COD)] (**30b**)*

To a yellow suspension of $[Pt_2(\mu\text{-}Cl)_2R_2(tht)_2]$ (0.15 g, 0.145 mmol) in $CHCl_3$ (30 ml) was added COD (106 μl, 0.864 mmol), and the mixture was stirred for 1 h. The resulting colorless solution was evaporated to dryness and the residue was triturated with Et_2O (8 ml), filtered, washed with Et_2O (3 ml) and air-dried (**30b**, 40%). The Et_2O solution was evaporated to dryness and the residue stirred with *n*-pentane affording a solid that was identified as a mixture of **26b** and a small amount of **30b**.

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References

[1] P.M. Maitlis, P. Espinet, M.J.H. Russell, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, Vol. 6, Chap. 38.4, Pergamon, Oxford, 1982.
[2] R. Usón, J. Forniés, Adv. Organomet. Chem. 28 (1988) 219.
[3] A.J. Canty, in E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, Vol. 9, Chap. 5, Pergamon, Oxford, 1995.
[4] G.B. Deacon, B.M. Gatehouse, K.T. Nelson-Reed, J. Organomet. Chem. 359 (1989) 267.
[5] G. López, G. García, M.D. Santana, G. Sánchez, J. Ruiz, J.A. Hermoso, A. Vegas, M. Martínez-Ripoll, J. Chem. Soc., Dalton Trans. (1990) 1621.
[6] G. López, G. García, G. Sánchez, M.D. Santana, J. Ruiz, J. García, Inorg. Chim. Acta 188 (1991) 200.
[7] C. Bartolomé, P. Espinet, F. Villafañe, S. Giesa, A. Martín, A. Guy Orpen, Organometallics 15 (1996) 2019.
[8] A.C. Albéniz, P. Espinet, Y. Jeannin, M. Philoche-Levisalles, B.E. Mann, J. Am. Chem. Soc. 112 (1990) 6594.
[9] A.C. Albéniz, P. Espinet, Organometallics 10 (1991) 2987.
[10] A.C. Albéniz, P. Espinet, Y.-S. Lin, Organometallics 14 (1995) 2977.
[11] A.C. Albéniz, P. Espinet, Y.-S. Lin, J. Am. Chem. Soc. 118 (1996) 7145.
[12] J.A. Casares, S. Coco, P. Espinet, Y.-S. Lin, Organometallics 14 (1995) 3058.
[13] J.A. Casares, P. Espinet, J.M. Martínez-Ilarduya, Y.-S. Lin, Organometallics 16 (1997) 770.
[14] R. Usón, J. Forniés, in: R.B. King, J.J. Eisch (Eds.), Organometallic Syntheses, Vol. 3, Elsevier, Amsterdam, 1986, pp. 161–185.
[15] R. Usón, J. Forniés, F. Martinez, M. Tomás, J. Chem. Soc., Dalton Trans. (1980) 888.
[16] R. Usón, J. Forniés, F. Martinez, M. Tomás, I. Reoyo, Organometallics 2 (1983) 1386.
[17] R. Usón, J. Forniés, M. Tomás, B. Menjón, Organometallics 4 (1985) 1912.
[18] R. Usón, J. Forniés, M. Tomás, B. Menjón, Organometallics 5 (1986) 1581.
[19] R. Usón, J. Forniés, R. Navarro, M.P. García, Inorg. Chim. Acta 33 (1979) 69.
[20] M.G. Hogben, W.A.G. Graham, J. Am. Chem. Soc. 91 (1969) 283.
[21] E.W. Abel, K.G. Orrell, A.G. Osborne, H.M. Pain, V. Sik, M.B. Hursthouse, K.M.A. Malik, J. Chem. Soc., Dalton Trans. (1994) 3441.
[22] F.T. Ladipo, G.K. Anderson, Organometallics 13 (1994) 303, and references therein.
[23] R. Usón, J. Forniés, M. Tomás, B. Menjón, C. Fortuño, A.J. Welch, D.E. Smith, J. Chem. Soc., Dalton Trans. (1993) 275.
[24] R. Usón, J. Forniés, M.A. Usón, S. Herrero, J. Organomet. Chem. 447 (1993) 137.
[25] J.M. Casas, L.R. Falvello, J. Forniés, A. Martín, Inorg. Chem. 35 (1996) 56.
[26] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd edn., Pergamon, Oxford, 1988.
[27] W.P. Weber, G.W. Gokel, I.K. Ugi, Angew. Chem., Int. Edn. Engl. 11 (1972) 530.
[28] D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 47.
[29] D. Drew, J.R. Doyle, Inorg. Synth. 28 (1990) 346.
[30] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6521.
[31] C.M. Harris, S.E. Livingstone, N.C. Stephenson, J. Chem. Soc. (1958) 3697.
[32] P.K. Byers, A.J. Canty, Organometallics 9 (1990) 210.