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Mono- and polynuclear complexes of palladium(II) and platinum(II) with $HC(PPh_2)_3$

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Abstract

Complexes of the type $[MXX'\{\eta^2\text{-}(PPh_2)_3CH\}]$ (M = Pd, X = X′ = Cl (**1**), Br (**3**), C_6F_5 (**6**); X = Cl, X′ = C_6F_5 (**4**); M = Pt X = X′ = Cl (**2**), C_6F_5 (**7**); X = Cl, X′ = C_6F_5 (**5**)) have been obtained by reaction of palladium or platinum compounds with $HC(PPh_2)_3$. The $^{31}P\{^1H\}$ NMR spectra of these complexes indicate that one of the P atoms of the triphosphine remains uncoordinated and allows the synthesis of polynuclear complexes such as $[(C_6F_5)_2M\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}Pt(C_6F_5)_2(CO)]$ (M = Pd (**9**), Pt (**10**)) and $[\{(C_6F_5)_2M(\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH)\}_2Au]$ (ClO_4) (M = Pd (**11**), Pt (**12**)). The structure of these complexes has been established using $^{31}P\{^1H\}$ and ^{19}F NMR spectra.

1. Introduction

There is a considerable interest in the use of the triphosphine 1,1,1-tris (diphenylphosphino) methane, $HC(PPh_2)_3$, tdppm, as a ligand [1] due to its versatile coordination behaviour. $HC(PPh_2)_3$ is ideally suited for the complexation of a trigonal array of metal atoms and this η^3–μ^3 coordination mode has been extensively studied [2]. Complexes in which $HC(PPh_2)_3$ acts as a η^1-monodentate [3], η^2-chelating [3,4], η^3-chelating [5], η^2-μ^2-bridging [3], and η^3-μ^2-bridging chelating agent [3,4b,6] have been characterized.

However, $HC(PPh_2)_3$ has received little attention in the context of palladium or platinum chemistry [4c,6a]. This paper deals with the systematic synthesis of several neutral or cationic palladium and platinum complexes containing tdppm acting as a chelate ligand, η^2-$HC(PPh_2)_3$, and their use for the preparation of polynuclear derivatives with the tdppm acting as a chelating bridging group, η^3-μ-$HC(PPh_2)_3$.

2. Results and discussion

Neutral mononuclear complexes of the type $[MXX'\{\eta^2\text{-}(PPh_2)_3CH\}]$ (X,X′ = Cl, Br, or C_6F_5; M = Pd or Pt) containing tris(diphenylphosphino)methane acting as a *P,P′*-bidentate ligand are obtained either by displacement reactions or bridge cleavage processes (eqns. (1)–(5)).

$$[MCl_2(THT)_2] + HC(PPh_2)_3 \xrightarrow{\text{acetone}} [MCl_2\{\eta^2\text{-}(PPh_2)_3CH\}] + 2THT \quad (1)$$

THT = tetrahydrothiophene, M = Pd (**1**), Pt (**2**)

$$[NBu_4]_2[Pd_2(\mu\text{-}Br)_2Br_4] + 2HC(PPh_2)_3 \xrightarrow{\text{acetone}} 2[PdBr_2\{\eta^2\text{-}(PPh_2)_3CH\}] + 2[NBu_4]Br \quad (2)$$

(**3**)

$$[\{M(\mu\text{-}Cl)(C_6F_5)(THT)\}_2] + 2HC(PPh_2)_3 \longrightarrow 2[MCl(C_6F_5)\{\eta^2\text{-}(PPh_2)_3CH\}] + 2THT \quad (3)$$

M = Pd (**4**), Pt (**5**)

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TABLE 1. Analytical [a] and conductivity [b] data for the complexes **1**–**12**

Complex		C (%)	H (%)	Λ_M
$[PdCl_2\{\eta^2\text{-}(PPh_2)_3CH\}]$	**1**	59.51 (59.58)	4.48 (4.19)	n.c.
$[PtCl_2\{\eta^2\text{-}(PPh_2)_3CH\}]$	**2**	53.45 (53.25)	3.68 (3.74)	n.c.
$[PdBr_2\{\eta^2\text{-}(PPh_2)_3CH\}]$	**3**	53.56 (53.23)	4.12 (3.74)	n.c.
$[PdCl(C_6F_5)\{\eta^2\text{-}(PPh_2)_3CH\}]$	**4**	59.01 (58.85)	4.41 (3.56)	n.c.
$[PtCl(C_6F_5)\{\eta^2\text{-}(PPh_2)_3CH\}]$	**5**	53.63 (53.45)	3.23 (3.23)	n.c.
$[Pd(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}]$	**6**	58.33 (58.32)	3.18 (3.09)	n.c.
$[Pt(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}]$	**7**	53.85 (53.61)	2.89 (2.84)	n.c.
$[Pd(C_6F_5)(PPh_3)\{\eta^2\text{-}(PPh_2)_3CH\}](ClO_4)$	**8**	61.44 (60.86)	4.30 (3.85)	116
$[(C_6F_5)_2Pd\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}Pt(C_6F_5)_2(CO)]$	**9**	47.92 (47.54)	2.25 (1.99)	n.c.
$[(C_6F_5)_2Pt\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}Pt(C_6F_5)_2(CO)]$	**10**	45.00 (44.99)	1.87 (1.88)	n.c.
$[\{(C_6F_5)_2Pd\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}\}_2Au](ClO_4)$	**11**	49.94 (50.85)	2.87 (2.70)	112
$[\{(C_6F_5)_2Pt\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}\}_2Au](ClO_4)$	**12**	46.26 (47.23)	2.66 (2.50)	100

[a] Calculated values in parentheses.

[b] in 5×10^{-4} M acetone solution, Λ_M in Ω^{-1} cm^2 mol^{-1}, (n.c. = non-conducting).

$$[NBu_4]_2\left[\{Pd(\mu\text{-}Cl)(C_6F_5)_2\}_2\right] + 2HC(PPh_2)_3 \longrightarrow 2\left[Pd(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}\right] + 2(NBu_4)Cl \quad (4)$$

$$(\mathbf{6})$$

$$\left[Pt(C_6F_5)_2(THT)_2\right] + HC(PPh_2)_3 \longrightarrow \left[Pt(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}\right] + 2THF \quad (5)$$

$$(\mathbf{7})$$

THF = tetrahydrofuran

The reaction between $[NBu_4]_2[\{Pt(\mu\text{-}Cl)_2(C_6F_5)_2\}_2]$ and $HC(PPh_2)_3$ does not yield a platinum complex homologous to the palladium product of eqn. (4), and a mixture of complexes, which was not elucidated, was obtained. However, the required complex **7** was obtained by using $[Pt(C_6F_5)_2(THF)_2]$ (eqn. (5)).

In contrast a cationic complex $[Pd(C_6F_5)(PPh_3)\{\eta^2\text{-}(PPh_2)_3CH\}](ClO_4)$ (**8**) was prepared according to eqns. (6) and (7), by using $AgClO_4$ as a halide abstractor in acetone and by treating the resulting solution, after filtration of the AgCl formed, with tdppm (molar ratio 1 : 1).

$$\left[PdCl(C_6F_5)(PPh_3)_2\right] + AgClO_4 \longrightarrow \left[Pd(C_6F_5)(PPh_3)_2(\text{acetone})_x\right](ClO_4) + AgCl \quad (6)$$

$$\left[Pd(C_6F_5)(PPh_3)_2(\text{acetone})_x\right](ClO_4) + HC(PPh_2)_3 \longrightarrow \left[Pd(C_6F_5)(PPh_3)\{\eta^2\text{-}(PPh_2)_3CH\}\right](ClO_4) + PPh_3 \quad (7)$$

$$(\mathbf{8})$$

TABLE 2. IR data (cm^{-1}) for the complexes **1**–**12**

Complex	C_6F_5	$HC(PPh_2)_3$	Others
1		550, 510, 505, 485, 475	300, 285 [a]
2		555, 515, 505, 490, 480	308, 285 [a]
3		550, 545, 515, 505, 485, 475	250, 245 [a]
4	1498, 951	541, 520, 503, 487, 471	303 [a]
5	1502, 954	553, 508, 494, 467	309 [a]
6	1497, 955	530, 510, 497, 490, 470	
7	1499, 956	554, 543, 520, 500, 495	
8	1500, 955	[d]	1100, 623 [b]
9	1512, 1502, 962, 952	585, 512, 500, 482	2115 [c]
10	1500, 970, 960	588, 546, 530, 523, 514, 502, 487	2089 [c]
11	1505, 957	532, 498, 483	1100, 624 [b]
12	1501, 959	543, 526, 504, 479	1100, 624 [b]

[a] $\nu(M-X)$.

[b] ClO_4^-.

[c] $\nu(CO)$ in $c[Pt(C_6F_5)_2(CO)(THF)]$: 2124 cm^{-1}.

[d] PPh_3 and $HC(PPh_2)_3$ bands overlap precluding an unambiguous assignment.

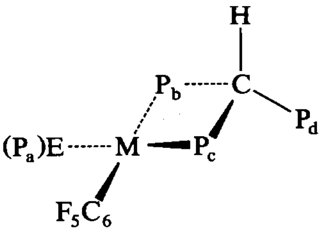


Fig. 1.

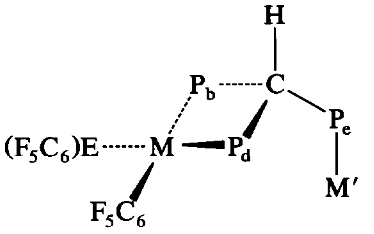


Fig. 2.

The formation of **8** takes place with displacement of one mole of PPh_3.

Finally, since all these complexes contain an uncoordinated P atom, they can be used for the synthesis of polynuclear complexes with a η^3-μ^2-$HC(PPh_2)_3$ group. Thus the treatment of $[M(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}]$ (M = Pd or Pt) with $[Pt(C_6F_5)_2(CO)(THF)]$ in CH_2Cl_2 gives binuclear neutral complexes (eqn. (8)).

$$[M(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}] + [Pt(C_6F_5)_2(CO)(THF)] \longrightarrow [(C_6F_5)_2M\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}Pt(C_6F_5)_2(CO)] \quad (8)$$

M = Pd (**9**), Pt (**10**)

The reaction of $[M(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}]$ with $[Au(tht)_2](ClO_4)$ in CH_2Cl_2 (molar ratio 2:1) leads to trinuclear cationic derivatives of the type $[\{(C_6F_5)_2M\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}\}_2Au](ClO_4)$ (M = Pd or Pt) (eqn. (9)).

$$2[M(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}] + [Au(THT)_2](ClO_4) \longrightarrow [\{(C_6F_5)_2M\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}\}_2Au](ClO_4) \quad (9)$$

M = Pd (**11**), Pt (**12**)

Analytical and conductivity data are collected in Table 1.

2.1. *IR spectra*

Selected IR data are collected in Table 2. Characteristic absorptions due to the C_6F_5 group are observed in complexes **4–12** (1510–1490vs; 970–950vs; 810–760s), the latter two sets assigned to the X-sensitive mode of the C_6F_5 group, have been used previously for structural assignments [7,8]. However, internal absorptions of the $HC(PPh_2)_3$ in this range render them useless in these complexes. Complexes **1–5** show bands in the region 310–245 cm^{-1} assignable to ν(M–X)(X = Cl: **1**, **2**, **4** and **5**; X = Br: **3**). Complexes **1**, **2** and **3** show two absorptions as expected for a *cis*-compound. Internal absorptions of other ligands have been assigned in Table 2. In complexes **9** and **10** the decrease of ν(CO) relative to that of the starting material indicates an increase of electron density around the platinum, in keeping with the higher basicity of the phosphine as compared to THF.

2.2. *NMR spectra*

2.2.1. *$^{31}P\{^1H\}$ NMR spectra*

Chemical shifts are presented in Table 3. For complexes **1–12** several types of P atom can be distinguished (Figs. 1 and 2). These are listed below.

a) P_a : P atom of the coordinate PPh_3;

b) P_b : P atom *trans* to a C_6F_5 group of tdppm;

c) P_c : P atom *trans* to a non-C_6F_5 group (E) of tdppm;

d) P_d : uncoordinated P atom of tdppm;

e) P_e : P atom (initially P_d) attached to a second metal centre (M′) (Fig. 2).

The P atoms of the η^2-$(PPh_2)_3CH$ group (P_b, P_c P_d) show high field ^{31}P chemical shifts (−18 to −39 ppm.).

TABLE 3. $^{31}P\{^1H\}$ NMR data [a]

Complex	P_a	P_b	P_c	P_d	P_e	$^2J(P_a\text{–}P_c)$	$^2J(P_b\text{–}P_c)$	$^2J(P_b\text{–}P_d)$	$^2J(P_c\text{–}P_d)$	$^1J(Pt\text{–}P_b)$	$^1J(Pt\text{–}P_c)$	$^1J(Pt\text{–}P_e)$	$^3J(Pt\text{–}P_b)$	$^3J(Pt\text{–}P_d)$
4		−36.05	−18.37	−24.35			99	17	21					
5		−36.55	−39.53	−24.59			68	18	24	1877	3360			
6		−20.97		−23.16				15						
7		−35.20		−22.01				16		2018				54
8	21.41	−26.32	−17.14	−18.76		398	88	14	14					
9		2.04			16.19							2159		
10		−8.72			17.30					2043		2160	189	
11		−13.45			30.59									
12		−9.94			47.53					2000			96	

[a] δ, ppm referred to H_3PO_4 85%, J in Hz, solvent $CDCl_3$; complexes **1**, **2** and **3** were not soluble enough for NMR measurements.

TABLE 4. ^{19}F NMR data [a] at room temperature

Complex	F_o	F_m	F_p	$^3J(Pt-F_o)$
4	−117.25	−163.67	−161.30	
5	−119.16	−164.41	−162.08	264.3
6	−116.22	−164.91	−162.73	
7	−116.00	−164.88	−163.13	312.0
8	−116.57	−162.01	−159.77	
	−117.53	−162.89		
9	−115.27	−163.45	−161.16	
	−118.43	−162.32	−158.02	332
			−159.55	
10	−117.97	−162.50	−157.59	260
	−118.56	−164.22	−159.69	327
			−161.99	
11	−113.66	−163.00	−160.49	
12	−116.27	−164.31	−162.35	317

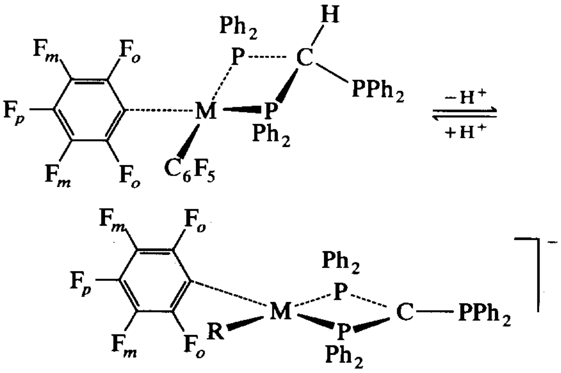
[a] δ, ppm referred to $CFCl_3$; J in Hz,; solvent $CDCl_3$; room temperature.

The $^2J(P_b-P_c)$ values are in the range 69–99 Hz, higher than the values of $^2J(P_b-P_d)$ and $^2J(P_c-P_d)$ (14–24 Hz). In the polynuclear derivatives **9–12**, with the triphosphine acting as bridging ligand, (η^3-μ^2-$(PPh_2)_3CH$), all the ^{31}P signals are shifted downfield relative to those in the mononuclear starting materials (**6**, **7**), with the highest variation corresponding to shift of P_e relative to P_d. The atoms labelled as P_e show low field ^{31}P chemical shifts, as does the P atom of the monodentate PPh_3 in complex (**8**).

2.2.2. ^{19}F NMR spectra

The neutral mononuclear complexes $[MX(C_6F_5)\{\eta^2\text{-}(PPh_2)_3CH\}]$ (M = Pd or Pt; X = Cl or C_6F_5) (**4–7**)) show ^{19}F NMR spectra at room temperature (Table 4) with three sets of signals corresponding to F_o, F_p and F_m, in keeping with the presence of one C_6F_5 group (**4**, **5**) or two equivalent C_6F_5 groups (**6**, **7**), in which both halves of each C_6F_5 group act as equivalent (AA′MXX′ system). At −85°C signals due to F_o and F_m are split (see Table 5) and the ^{19}F NMR spectra are as expected for an AFMRX system, which corresponds to the static molecule. However, if it is assumed that the C_6F_5 groups are not able to rotate around the $M-C_{ipso}$ bonds because of steric hindrance [9], a dynamic process on the NMR time scale should be operating at room temperature in order effectively to produce a plane of symmetry. Nevertheless, we have not found a sensible explanation for our observations since the two more obvious of these processes (a) deprotonation/protonation of the acidic H atom of the tdppm and (b) fast intramolecular exchange of the coordinated and uncoordinated P atoms of the tdppm, must be excluded for the following reasons:

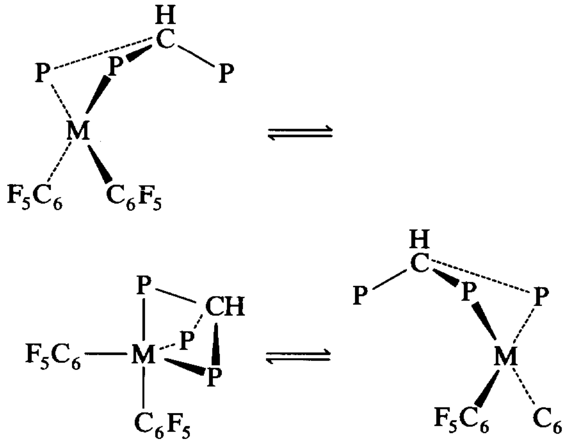
a) A dynamic process such as that presented in eqn. (10) seems not to operate since the ^1H NMR spectra of the complexes at room temperature show a sharp quartet (5–6 ppm.) assigned [4d] to the H atom of $HC(PPh_2)_3$ coupled with the three ^{31}P nucleus. The $^2J(P-H)$ coupling constants are almost the same. (See Experimental section.)



(10)

R = C_6F_5

b) Fast intramolecular exchange of P atoms (eqn. (11)) would imply the equivalence of all P atoms of the $HC(PPh_2)_3$. However, the $^{31}P\{^1H\}$ NMR spectra in $(CD_3)_2SO$ remain unchanged, even at 60°C for complexes **4** and **5** and at 120°C for complexes **6** and **7**, and continue to show three (**4**, **5**) or two (**6**, **7**) types of chemically inequivalent ^{31}P nucleus, consistent with a static structure.



(11)

The ^{19}F NMR spectra of the cationic trinuclear complexes $[\{(C_6F_5)_2M(\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH)\}_2Au](ClO_4)$ (M = Pd (**11**), Pt (**12**) are similar to those of (**4–7**) (Table 5).

The ^{19}F NMR spectrum of $[Pd(C_6F_5)(PPh_3)\{\eta^2\text{-}(PPh_2)_3CH\}](ClO_4)$ (**8**) shows two signals due to F_o atoms, two due to F_m and one due to F_p, thus indicating that the two halves of the C_6F_5 group are inequivalent.

The ^{19}F NMR spectra of the neutral dinuclear derivatives $[(C_6F_5)_2M\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}Pt(C_6F_5)_2\text{-}$

TABLE 5. ^{19}F NMR data [a] at low temperature

Complex	F_o	F_m	F_p	$^3J(Pt-F_o)$
4	−116.51	−162.41	−160.43	
	−118.75	−162.74		
5	−118.72	−162.92	−161.15	254.8
	−120.68	−163.36		238.2
6	−113.09	−162.75	−161.12	
	−113.85	−163.05		
7	−118.28	−164.06 [b]	−162.26	[c]
	−118.78			
11	−110.40	−160.00	−159.60	
	−111.71	−160.21		
12	−113.19	−161.82	−160.37	[c]
	−114.27	−162.72		

[a] δ, ppm referred to $CFCl_3$; J in Hz.; solvent CD_2Cl_2; −85°C.

[b] broad signal.

[c] Signals partially overlap, precluding the measurement of the coupling constant $^3J(Pt-P_o)$.

(CO)] M = Pd (**9**), Pt (**10**) show three signals corresponding to F_p atoms, one of them with double the intensity of the other two. This indicates that there are three types of C_6F_5 group, in keeping with the proposed formulae. However, a complete assignment of signals due to F_o and F_m atoms of the different types of C_6F_5 group cannot be made because of some overlapping of signals. For $[(C_6F_5)_2Pd\{\eta^3-\mu^2-(PPh_2)_3CH\}Pt(C_6F_5)_2(CO)]$ (**9**), one signal due to F_o atoms of the C_6F_5 groups bonded to palladium can clearly be observed, and a complex multiplet with ^{195}Pt satellites (with the same fine structure as the main signal) can be observed for the F_o atoms of the two different types of C_6F_5 group bonded to platinum. Signals due to all F_m atoms appears as two complex multiplets (see Table 4). For complex **10**, only two signals (with ^{195}Pt satellites) due to F_o atoms are observed as well as two broad signals due to the F_m atoms.

3. Experimental section

C and H analyses, IR spectra, ^{1}H, ^{19}F and ^{31}P{^{1}H} NMR spectra and conductance data were obtained as described previously [10]. The starting materials $[\{Pd(\mu-Cl)(C_6F_5)(THT)\}_2]$ [11], $[\{Pt(\mu-Cl)(C_6F_5)(THT)\}_2]$ [12], $[PtCl_2(THT)_2]$ [12,13] $[PdCl_2(THT)_2]$ [13], $(NBu_4)_2[\{Pd(\mu-Cl)(C_6F_5)_2\}_2]$ [13], $[NBu_4]_2[\{Pd(\mu-Br)Br_2\}_2]$ [14] *cis*-$[Pt(C_6F_5)_2(THF)_2]$ [15], *trans*-$[PdCl(C_6F_5)(PPh_3)_2]$ [16], *cis*-$[Pt(C_6F_5)_2(CO)(THF)]$ [17] and $[Au(THT)_2](ClO_4)$ [18] were prepared by published methods.

3.1. $[MCl_2\{\eta^2-(PPh_2)_3CH\}]$; M = Pd (1), Pt (2)

To a solution of $[PdCl_2(THT)_2]$ (0.200 g, 0.565 mmol) in acetone (30 ml) at room temperature, $HC(PPh_2)_3$ (0.321 g, 0.565 mmol) was added. The initially deep orange solution turned pale yellow and a pale yellow solid precipitated; the suspension was stirred for 1 h at room temperature and then the precipitate was filtered off and washed with acetone (3 × 5 ml). **1**: 0.39 g, 92% yield. Complex **2** was obtained similarly from $[PtCl_2(THT)_2]$ (0.353 g, 0.802 mmol) and $HC(PPh_2)_3$ (0.456 g, 0.802 mmol). **2**: 0.54 g, 80% yield.

3.2. $[MBr_2\{\eta^2-(PPh_2)_3CH\}]$ (3)

Complex **3** was obtained similarly to **1**, **2** from $(NBu_4)_2[\{Pd(\mu-Br)Br_2\}_2]$ (0.25 g, 0.164 mmol) and $HC(PPh_2)_3$ (0.186 g, 0.328 mmol). **3**: 0.25 g, 75% yield.

3.3. $[MCl(C_6F_5)\{\eta^2-(PPh_2)_3CH\}]$; M = Pd (4), Pt (5)

To a solution of $[\{Pd(\mu-Cl)(C_6F_5)(THT)\}_2]$ (0.42 g, 0.528 mmol) in benzene (30 ml) $HC(PPh_2)_3$ (0.601 g, 1.057 mmol) was added. The mixture was stirred for 30 min at 25°C. The resulting precipitate was filtered off and washed with Et_2O (2 × 10 ml). **4**: 0.9 g, 97% yield. ^{1}H NMR data ($CDCl_3$, 20°C): $\delta[HC(PPh_2)_3]$: 5.57 ppm. $^2J(P-H)$ = 8.7 Hz. Complex **5** was obtained similarly from $[\{Pt(\mu-Cl)(C_6F_5)(THT)\}_2]$ (1.00 g, 1.04 mmol) and $HC(PPh_2)_3$ (1.1814 g, 2.08 mmol). **5**: 1.37 g, 70% yield. ^{1}H NMR ($CDCl_3$, 20°C): δ $[HC(PPh_2)_3]$: 5.66 ppm $^2J(P-H)$ = 7.6 Hz.

3.4. $[Pd(C_6F_5)_2\{\eta^2-(PPh_2)_3CH\}]$ (6)

To an acetone solution (30 ml) of $[NBu_4]_2[\{Pd(\mu-Cl)(C_6F_5)_2\}_2]$ (0.9 g, 0.626 mmol) $HC(PPh_2)_3$ (0.712 g, 1.252 mmol) was added. The mixture was stirred for 3 h at room temperature. After evaporating to small volume (2 ml) and addition of ^{i}PrOH (20 ml), a white solid **6**, which was washed with hexane (2 × 10 ml), was obtained: 0.632 g, 50% yield. ^{1}H NMR ($CDCl_3$, 20°C): $\delta[HC(PPh_2)_3]$: 5.49 ppm $^2J(P-H)$ = 10.0 Hz.

3.5. $[Pt(C_6F_5)_2\{\eta^2-(PPh_2)_3CH\}]$ (7)

To a solution of $Pt(C_6F_5)_2(THF)_2$ (0.5 g, 0.742 mmol) in acetone (20 ml), $HC(PPh_2)_3$ (0.422 g, 0.742 mmol) was added, and the mixture was stirred at room temperature for 10 min. The solution was evaporated to dryness and the resulting oily residue was treated with Et_2O (20 ml), giving a white solid **6**: 0.448 g, 55% yield. ^{1}H NMR ($CDCl_3$, 20°C): $\delta[HC(PPh_2)_3]$: 5.56 ppm $^2J(P-H)$ = 9.0 Hz.

3.6. $[Pd(C_6F_5)(PPh_3)\{\eta^2-(PPh_2)_3CH\}](ClO_4)$ (8)

$[PdCl(C_6F_5)(PPh_3)_2]$ (0.150 g, 0.180 mmol) was treated with $AgClO_4$ (0.037 g, 0.180 mmol) in acetone (30 ml). After stirring for 30 min at room temperature, the precipitated AgCl was filtered off. To the acetone solution, $HC(PPh_2)_3$ (0.102 g, 0.180 mmol) was added, and the mixture was heated under reflux for 2 h and then evaporated to small volume (2 ml). The addition of Et_2O (25 ml) gave a pale yellow solid **8**: 0.16 g, 74% yield.

3.7. $[(C_6F_5)_2M\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}Pt(C_6F_5)_2(CO)]$; M = Pd (9), Pt (10)

To a solution of $[Pd(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}]$ (**6**) (0.160 g, 0.158 mmol) in CH_2Cl_2 (20 ml), $[Pt(C_6F_5)_2(CO)(THF)]$ (0.100 g, 0.158 mmol) was added. The mixture was stirred at room temperature for 1.5 h and then evaporated to small volume (2 ml). The addition of hexane (20 ml) gave a white solid **9**: 0.2025 g, 82% yield. Complex **10** was obtained similarly from $[Pt(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}]$ (**7**) (0.22 g, 0.200 mmol) and $[Pt(C_6F_5)_2(CO)(THF)]$ (0.144 g, 0.200 mmol). **10**: 0.265 g, 80% yield.

3.8. $[\{(C_6F_5)_2M\{\eta^3\text{-}\mu^2\text{-}(PPh_2)_3CH\}\}_2Au](ClO_4)$; M = Pd (11), Pt (12)

The treatment of [AuCl(THT)] (0.063 g, 0.198 mmol) with $[Ag(OClO_3)(THT)]$ (0.058 g, 0.198 mmol) in CH_2Cl_2 (20 ml) (30 min, room temperature) gave a solution of $[Au(THT)_2](ClO_4)$ after filtration of precipitated AgCl. To this solution was added $[Pd(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}]$ (**6**) (0.400 g, 0.396 mmol). The mixture was stirred for 30 min at room temperature and evaporated to dryness; the addition of Et_2O (25 ml) gave a pale yellow solid (**11**): 0.3417 g, 75% yield. Complex **12** was obtained similarly from [AuCl(THT)] (0.0146 g, 0.0455 mmol), $[Ag(OClO_3)(THT)]$ (0.0134 g, 0.0455 mmol) and $[Pt(C_6F_5)_2\{\eta^2\text{-}(PPh_2)_3CH\}]$ (**7**) (0.100 g, 0.091 mmol). (**12**): 0.0678 g, 60% yield.

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