Synthesis and characterization of neutral and anionic carbonyl derivatives of palladium(II)†‡

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The action of CO on the solvento-complexes *cis*-[PdR$_2$(thf)$_2$] [R = C$_6$F$_5$ (**1**), C$_6$Cl$_5$ (**2**)] at low temperature gives *cis*-[PdR$_2$(CO)$_2$] [R = C$_6$F$_5$ (**3**), C$_6$Cl$_5$ (**4**)] in good yield by simple replacement of the highly labile thf molecules. These are rare cases of Pd^{II} dicarbonyl compounds, whose characterization relies on spectroscopic and analytic data. The crystal structure of the square-planar platinum homologue *cis*-[Pt(C$_6$Cl$_5$)$_2$(CO)$_2$] is also presented. CO can split the double bridging-system in the dinuclear species [{PdR$_2$}$_2$(μ-X)$_2$]$^{2-}$ giving the homologous series of anionic monocarbonyl Pd^{II} derivatives with formula [*cis*-PdR$_2$X(CO)]$^-$ (**5–10**: R = C$_6$F$_5$, C$_6$Cl$_5$; X = Cl, Br, I), which were isolated (except for the R = C$_6$F$_5$ and X = I) and suitably characterized. Characterization includes the crystal and molecular structure of [PPh$_3$Me][*cis*-Pd(C$_6$F$_5$)$_2$Br(CO)] (**6′**). The anionic species [NBu$_4$][*cis*-Pd(C$_6$F$_5$)$_2$Cl(CO)] (**5**) reacts with neutral *cis*-[Pd(C$_6$F$_5$)$_2$(CO)$_2$] (**3**) under CO extrusion, affording the dinuclear derivative [NBu$_4$][{Pd(C$_6$F$_5$)$_2$(CO)}$_2$(μ-Cl)] (**11**), which contains a single unsupported halide bridge (X-ray diffraction). Complex **11** can be considered as modelling a possible intermediate step in intermolecular CO substitution reactions that are easily undergone by Pd^{II} halo carbonyl species.

Introduction

The synthesis and characterization of palladium(II) carbonyl derivatives as well as the study of their physical and chemical properties have attracted the attention of chemical researchers for a very long time.[1] Shortly after the preparation of the first metal carbonyl derivatives, *cis*-[PtCl$_2$(CO)$_2$] and [{PtCl(CO)}$_2$(μ-Cl)$_2$] by Schützenberger in the late 19th century,[2] an extension to the lighter element Pd was naturally attempted. Early reports on the synthesis of the analogous Pd carbonyl compounds,[3] however, were later found to be erroneous.[4] One of the factors causing confusion in the identification of the resulting derivatives was the ease with which Pd^{II} compounds are reduced by CO, especially in the presence of moisture.[5] The dinuclear compound [{PdCl(CO)}$_2$(μ-Cl)$_2$] was eventually obtained,[6] but, to the best of our knowledge, the mononuclear compound *cis*-[PdCl$_2$(CO)$_2$] has still not been isolated. The main reason for this failure is the expected high lability of the Pd–CO bond in the latter compound, which would readily undergo substitution reactions. Since metal-coordinated halo ligands, M–X, still show a considerable nucleophilic character, revealed, for instance, in their ability to build [3c,4e]-bridges, the range of stability of the mononuclear species relative to the dinuclear one would be very narrow (if any). In fact, the synthesis of the dicarbonyl derivative *cis*-[Pd(OSO$_2$F)$_2$(CO)$_2$],[7] as well as that of the singular and highly electrophilic homoleptic species[8] [Pd(CO)$_4$][Sb$_2$F$_{11}$]$_2$ was only possible in superacidic media and in the absence of even moderate nucleophiles.

The low nucleophilicity of the metal-bound C$_6$F$_5$ and C$_6$Cl$_5$ groups (R) also allowed us to isolate the dicarbonyl compounds *cis*-[PdR$_2$(CO)$_2$], as has been briefly communicated.[9] The same principle was applied in the synthesis of a series of all-organometallic analogues of Zeise's salt with formula [NBu$_4$][M(C$_6$F$_5$)$_3$(η^2-C$_2$H$_4$)] for all three Group 10 metals (M = Ni, Pd, Pt).[10] The recent synthesis of a family of square-planar nickel(II) carbonyl compounds with formula [NBu$_4$][*cis*-Ni(C$_6$F$_5$)$_2$X(CO)] (X = Cl, Br, I)[11] has prompted us to complete the series of Group 10 metal carbonyl species by preparing the corresponding derivatives of Pd^{II}. In this paper we report on the synthesis and characterization of a series of neutral and anionic carbonyl derivatives of palladium(II) containing ligands of moderate and/or reduced nucleophilic character.

Synthesis and characterization of *cis*-[PdR$_2$(thf)$_2$]

The solvento-complexes *cis*-[PdR$_2$(thf)$_2$] [R = C$_6$F$_5$ (**1**), C$_6$Cl$_5$ (**2**)] are obtained by 1 : 2 reaction of the corresponding dinuclear precursors [NBu$_4$]$_2$[{PdR$_2$}$_2$(μ-X)$_2$] with AgClO$_4$ in thf under light exclusion (Scheme 1). Compounds **1** and **2** are efficiently separated from the accompanying [NBu$_4$]ClO$_4$ salt by Et$_2$O extraction. This is a key step in the isolation of **1** and **2** as pure solids. Attempts to use safer silver salts, AgY (Y = SO$_3$CF$_3$, BF$_4$, PF$_6$), gave samples of **1** and **2** contaminated with varying amounts of [NBu$_4$]Y salts due to their appreciable solubilities in Et$_2$O. Although ineffective when aiming to obtain pure samples of **1** and **2**, these AgY salts can still be used to prepare solutions of *cis*-[PdR$_2$(thf)$_2$]. Such thf solutions of **1** and **2** are equally well suited as *in situ* prepared reagents for many synthetic purposes.

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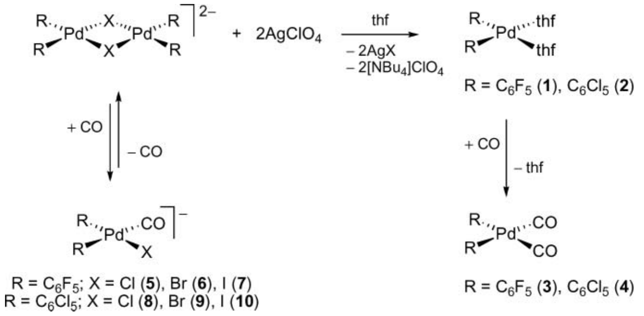

Scheme 1 Syntheses of solvento compounds **1** and **2** and mononuclear carbonyl derivatives **3–10** of perhalophenyl-palladium(II). The anionic species were isolated as their corresponding $[NBu_4]^+$ salts.

Compounds **1** and **2** have been identified by analytical and spectroscopic methods (IR and NMR). The crystal and molecular structures of **1** have also been established by single-crystal X-ray diffraction methods. The Pd atom is in a slightly distorted square-planar (*SP*-4) environment with the ligands adopting a *cis* disposition (Fig. 1). The Pd–O distances compare well with those found in other neutral thf complexes of Pd^{II}, such as $[Pd\{(PPh_2CH_2)_2BPh_2\text{-}\kappa^2P\}(OSO_2CF_3)(thf)]$ (Pd–O 215.7(2) pm)[12] or *trans*-$[PdCl_2(L)(thf)]$ (Pd–O 211.2(2) pm; L = 2,6,7-trioxa-3,5,8-tris(trichloromethyl)-1,4-diphosphabicyclo[2.2.2]octane).[13] Shorter Pd–O distances were found in $[Pd(phen)(thf)_2](NO_3)_2$ (average Pd–O 202.2(8) pm),[14] a fact that can be related to the cationic nature of the metal complex. On the other hand, the longer Pd–O bond length found in the dinuclear Pd^I compound $[(Ph_3P)Pd(\mu\text{-}PPh_2NHPPh_2)_2Pd(thf)][BF_4]$ (Pd–O 229.8(8) pm)[15] can be attributed to the expected increase in size of the metal ion on reduction. The Pd–C distances in **1** do not significantly deviate from the standard value assigned to a Pd^{II}–C(aryl) bond (198.1 pm).[16] Acute C^{ortho}–C^{ipso}–C^{ortho} angles are observed in the C_6F_5 rings, as are usually found wherever electron-withdrawing perhalophenyl groups are bound to more electropositive centres.[17]

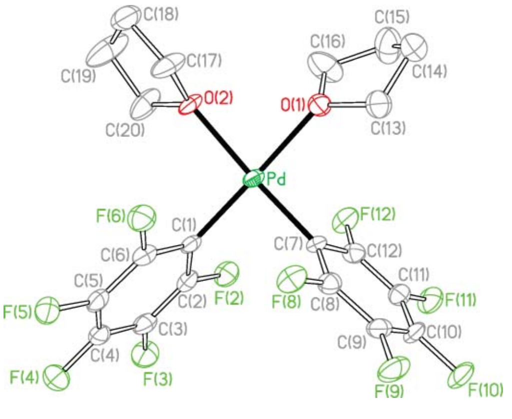

Fig. 1 Thermal ellipsoid diagram (50% probability) of **1**. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Pd–C(1) 197.6(4), Pd–C(7) 196.2(4), Pd–O(1) 212.1(3), Pd–O(2) 212.0(3), C(1)–C(2) 137.3(6), C(1)–C(6) 138.1(6), C(7)–C(8) 136.9(6), C(7)–C(12) 139.3(6), C(1)–Pd–C(7) 87.48(16), C(1)–Pd–O(1) 177.31(12), C(1)–Pd–O(2) 95.59(14), C(7)–Pd–O(1) 93.93(14), C(7)–Pd–O(2) 176.57(12), O(1)–Pd–O(2) 83.06(11), Pd–C(1)–C(2) 124.6(3), Pd–C(1)–C(6) 120.6(3), C(2)–C(1)–C(6) 114.8(4), Pd–C(7)–C(8) 123.8(3), Pd–C(7)–C(12) 121.5(3), C(8)–C(7)–C(12) 114.6(4).

This feature will also appear in the remaining structures reported in the present work but will not be mentioned further. The C_6F_5 rings are moderately tilted, forming a dihedral angle of *ca.* 70° with the coordination plane. The overall geometric arrangement in **1** is similar to that found in the lighter homologous species *cis*-$[Ni(C_6F_5)_2(thf)_2]$,[11] with Pd–ligand bond lengths *ca.* 15 pm longer than the corresponding Ni–ligand ones, according to the different radii assigned to Ni^{II} and Pd^{II} in *SP*-4 environments.[18]

Synthesis and characterization of *cis*-$[PdR_2(CO)_2]$

The thf molecules in **1** and **2** are labile and can be easily replaced by a number of ligands and metalloligands[19] and thus, compounds **1** and **2** behave as useful synthons of the "PdR_2" fragments. Moreover, those synthons usually retain their *cis* stereochemistry along the processes undergone. In line with this behaviour, CO also replaces the thf ligands at **1** and **2** affording *cis*-$[PdR_2(CO)_2]$ [R = C_6F_5 (**3**), C_6Cl_5 (**4**)] (Scheme 1). The reactions proceed in good yields and without metal reduction as long as moisture is rigorously excluded from the reaction medium. Otherwise, formation of finely divided black Pd metal is observed and the yields are lowered accordingly.

Compounds *cis*-$[PdR_2(CO)_2]$ [R = C_6F_5 (**3**), C_6Cl_5 (**4**)] belong to the rare class of Pd^{II} dicarbonyl derivatives, for which just a single additional example is known: *cis*-$[Pd(OSO_2F)_2(CO)_2]$.[7] The latter compound was obtained by reductive carbonylation of the mixed-valence salt $Pd^{II}Pd^{IV}(SO_3F)_6$ in fluorosulfuric acid as the solvent, following a complex multistep procedure, which involves various associated redox and rearrangement processes. This is in contrast with the mild conditions under which compounds **3** and **4** are straightforwardly obtained (stereoselective ligand replacement in non-coordinating organic solvents at low temperature). A key factor allowing the isolation of all these *cis*-$[PdR'_2(CO)_2]$ compounds is the low residual nucleophilicity of the R′ coligands (R′ = C_6F_5, C_6Cl_5 or SO_3F). The IR spectra of **3** and **4** show two sharp absorptions assignable to the symmetric and asymmetric vibration modes of the *cis*-$Pd(CO)_2$ unit (Table 1). Appreciably higher ν(CO) values are observed for the pentafluoro- (2186 and 2163 cm^{-1}) than for the pentachloro-phenyl derivative (2173 and 2152 cm^{-1}), according to the higher electron-withdrawing ability of C_6F_5 *vs.* C_6Cl_5.[11] Likewise, the much higher ν(CO) frequencies observed for *cis*-$[Pd(OSO_2F)_2(CO)_2]$ (2228 and 2208 cm^{-1})[7] denote that the Pd^{II} centre is considerably more acidic in the *cis*-$Pd(OSO_2F)_2$ fragment than in the *cis*-PdR_2 ones. This observation

Table 1 IR-active stretching ν(CO) frequencies [cm^{-1}] for the neutral and anionic carbonyl metal complexes with formulae *cis*-$[MR_2(CO)_2]$ and *cis*-$[MR_2X(CO)]^-$ (R = C_6F_5, C_6Cl_5) in CH_2Cl_2 solution

Formula	M = Ni[a]	M = Pd[b]	M = Pt[c]
cis-$[M(C_6F_5)_2(CO)_2]$	2162, 2138	2186, 2163	2174, 2143
cis-$[M(C_6Cl_5)_2(CO)_2]$	—	2173, 2152	2160, 2126
cis-$[M(C_6F_5)_2Cl(CO)]^-$	2090	2124	2091
cis-$[M(C_6F_5)_2Br(CO)]^-$	2084	2121	2087
cis-$[M(C_6F_5)_2I(CO)]^-$	2073	2114	—
cis-$[M(C_6Cl_5)_2Cl(CO)]^-$	—	2120	—
cis-$[M(C_6Cl_5)_2Br(CO)]^-$	—	2114	—
cis-$[M(C_6Cl_5)_2I(CO)]^-$	—	2109	2084

[a] Ref. 10. [b] This work. [c] Ref. 28.

is in agreement with the weak coordinating ability documented for the SO_3F^- ion.

We were not able to obtain good-quality single-crystals of compounds **3** or **4**, which would have been suitable for X-ray diffraction purposes. The molecular structure of **3** would, however, be expected to be roughly similar to that previously reported for the isoleptic and isoelectronic species *cis*-$[Ni(C_6F_5)_2(CO)_2]$,[11] taking into account the different radii of the metal centres in each case (see above). We now report the crystal and molecular structure of *cis*-$[Pt(C_6Cl_5)_2(CO)_2]\cdot 3H_2O$, which can be considered as a valid model for compound **4**. The metal atom is in an approximately *SP*-4 environment (Fig. 2), with the sum of the bond angles defined by the atoms directly bound to Pt amounting 360.1°. The molecule has a crystallographically imposed C_2 axis bisecting the $Pt(C_6Cl_5)_2$ and $Pt(CO)_2$ angles. The only crystallographically independent Pt–C_6Cl_5 distance (207.4(7) pm) is similar to those found in other *SP*-4 pentachlorophenyl-platinum(II) derivatives, such as $[NBu_4]_2[Pt(C_6Cl_5)_4]$ (average Pt–C 208.6(14) pm).[20] The C_6Cl_5 ring is tilted by 65.5° with respect to the coordination plane. The Pt–CO distance (196.7(8) pm) is similar to that found in the metallacyclic compound $[Pt(C\&C)(CO)_2]$ (average Pt–C(CO): 198(2) pm; C&C = biphenyl-2,2′-diyl)[21] and longer than those found in the remaining dicarbonyl derivatives of Pt^{II} for which the molecular structure has been established, *viz.* *cis*-$[Pt(OSO_2CF_3)_2(CO)_2]$ (average Pt–C: 188.2(3) pm)[22] and *cis*-$[PtCl_2(CO)_2]$ (average Pt–C: 189.7(5) pm).[23] The longer Pt–CO distances found in the former cases can be attributed to the higher *trans* influence of the aryl ligands with respect to the Cl or OSO_2F ones.[24] The Pt–C–O unit is virtually linear (178.0(9)°). The insensitivity of the C–O distance in metal carbonyl derivatives to the ν(CO) value and to the nature of the coligands had already been noted.[25]

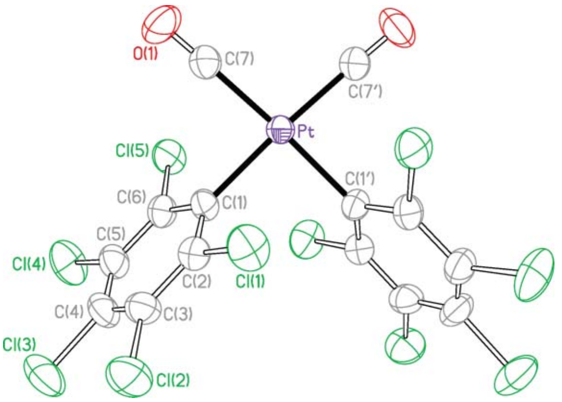

Fig. 2 Thermal ellipsoid diagram (50% probability) of *cis*-$[Pt(C_6Cl_5)_2(CO)_2]$ as found in single crystals of the trihydrate. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Pt–C(1) 207.4(7), Pt–C(7) 196.7(8), C(1)–C(2) 140.5(11), C(1)–C(6) 140.4(10), C(7)–O(1) 109.8(11), C(1)–Pt–C(1′) 90.3(4), C(1)–Pt–C(7) 86.7(3), C(1)–Pt–C(7′) 176.5(3), C(7)–Pt–C(7′) 96.4(5), Pt–C(1)–C(2) 123.9(5), Pt–C(1)–C(6) 120.0(6), C(2)–C(1)–C(6) 116.1(6), Pt–C(7)–O(1) 178.0(9).

In the crystal packing, the *cis*-$[Pt(C_6Cl_5)_2(CO)_2]$ molecules adopt an alternating zigzag arrangement along the *c* axis (Fig. 3), following a roughly similar pattern to that observed for the related species $[Pt(C\&C)(CO)_2]$[21] and *cis*-$[PtCl_2(CO)_2]$.[23] The bulkiness of the C_6Cl_5 groups, however, seems to preclude a closer approach of the Pt centres in our case. The observed intermetallic distance between adjacent metal atoms along the *c* axis is 0.61 nm and the Pt···Pt′···Pt″ angle (149.8°) largely deviates from linearity. Thus, neither the intermetallic distance nor the relative geometric disposition are appropriate to denote the existence of any extended interaction between the d^8 metal centres. The absence of intermolecular Pt···Pt interactions is in keeping with the lack of any observable pyramidalization within the individual molecules.[26] Loose intermolecular interactions are, however, observed between *ortho*-Cl atoms of the C_6Cl_5 group and the electrophilic C atom of the CO ligand with a Cl···C distance (340.8 pm) slightly shorter than the sum of the corresponding van der Waals radii (345 pm).[27] Intermolecular interactions between some neighbouring basic centres (in the Lewis sense) and the C atom of the CO ligand are frequently observed in metal carbonyl derivatives in which the CO molecule acts as a mainly σ-donor ligand.[7,22]

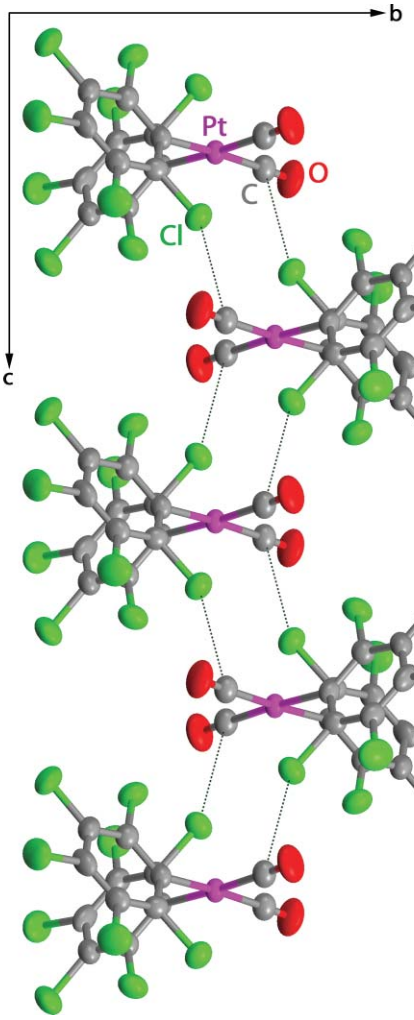

Fig. 3 Schematic diagram of the zigzag arrangement of *cis*-$[Pt(C_6Cl_5)_2(CO)_2]$ units along the *c* axis as found in single crystals of the trihydrate. Solvent molecules appear to be hydrogen-bonded between them (O···O separation: 0.26–0.28 nm) but, as they do not seem to interact with the organometallic unit, they have been omitted for clarity. Relevant intermolecular distances [pm] and angles [°]: $Cl^{ortho}\cdots C(CO)$ 340.8, Pt···Pt′···Pt″ 149.8.

Similar structural features would be expected for the isoleptic Pd^{II} compound **4** at molecular level. Perhaps, even a slightly longer Pd–CO bond length would be anticipated bearing in mind: (1) the comparable radii of the Pd^{2+} (64 pm) and Pt^{2+} (60 pm) ions in *SP*-4 environments,[18] and (2) the significantly higher ν(CO) value observed for the Pd derivative (Table 1). In fact, the Pd^{II} derivatives exhibit the highest ν(CO) values within the family of metal dicarbonyl compounds *cis*-$[MR_2(CO)_2]$ for all three Group 10 metals (M = Ni, Pd, Pt). It appears that Pd has a diminished ability to efficiently become involved in the π-back donation mechanism of the M–CO bond.

Synthesis and characterization of $[NBu_4][\textit{cis}\text{-}PdR_2X(CO)]$

The reaction of the dinuclear compounds $[NBu_4]_2[\{PdR_2\}_2(\mu\text{-}X)_2]$ (R = C_6F_5, C_6Cl_5; X = Cl, Br, I) with CO (1 atm) takes place in so-called "non-coordinating" solvents at room temperature under splitting of the double halide-bridging system (Scheme 1). Given the known precedents in the chemistry of perhalophenyl-derivatives of Ni and Pt,[11,28] it is sensible to assume that CO coordination also takes place with stereoretention in the Pd case. The whole series of monocarbonyl derivatives $[NBu_4][\textit{cis}\text{-}PdR_2X(CO)]$ (**5–10**) are observed to form in solution under a CO atmosphere (IR spectroscopy), but they revert to the corresponding parent species at reduced CO pressure. The intermolecular substitution process leading to the reversible formation of the starting materials can be prevented in all cases but one, by slow addition of a CO-saturated precipitating agent at low temperature (–78 °C). Under these conditions we succeeded in isolating compounds **5**, **6** and **8–10** (Scheme 1) in reasonable yields. Our attempts to isolate $[NBu_4][\textit{cis}\text{-}Pd(C_6F_5)_2I(CO)]$ (**7**) invariably led to the dinuclear compound $[NBu_4]_2[\{Pd(C_6F_5)_2\}_2(\mu\text{-}I)_2]$.

Compounds **5**, **6** and **8–10** have been identified by analytical and spectroscopic methods. The IR spectra of compounds **5–10** in solution show single, sharp absorptions in the 2100 cm^{-1} region (Table 1) corresponding to the only IR-active ν(CO) vibration mode. This spectroscopic behaviour is compatible with both possible *cis* and *trans* geometries. However, the presence of two equally intensive absorptions assignable to the X-sensitive vibration modes in the pentafluorophenyl derivatives **5** and **6** points to a *cis* arrangement, as initially assumed.§ An increase of *ca.* 5 cm^{-1} in the ν(CO) value is observed on changing the halogen in order of increasing electronegativity: I < Br < Cl. According to the behaviour observed in the dicarbonyl derivatives **3** and **4** (see above), slightly higher ν(CO) values are observed for the pentafluoro- than for the pentachloro-phenyl derivatives for a given halogen within the $[PdR_2X(CO)]^-$ series. The presence of two chemically inequivalent C_6F_5 groups in the ^{19}F NMR spectra of **5–7** in solution allows a *cis* geometry to be unambiguously assigned to this set of compounds. The low solubility of the perchlorophenyl compounds **8–10** in poorly coordinating organic solvents—especially at the low temperatures required to prevent their dimerisation under CO extrusion (Scheme 1)—precluded the acquisition of good-quality ^{13}C NMR spectra. However, the homogeneous variation by *ca.* 5 cm^{-1} in the ν(CO) value on changing the halogen observed in both the pentafluoro- and pentachloro-phenyl series noted above (Table 1), makes it sensible to assign a *cis* geometry to compounds **8–10**.

In order to confirm that the *cis* geometry is maintained in the solid state and also to enable a meaningful comparison with the known Ni homologous species,[11] the crystal and molecular structures of the salt $[PMePh_3][\textit{cis}\text{-}Pd(C_6F_5)_2Br(CO)]$ (**6′**) were established by X-ray diffraction methods. The $[PMePh_3][\textit{cis}\text{-}M(C_6F_5)_2Br(CO)]$ salts (M = Ni, Pd) were found to be isomorphous (triclinic, $P\bar{1}$) and isostructural. The angles around the Pd atom in the anion of **6′** (Fig. 4) are similar to those found in the Ni species. The metal–ligand bond lengths are longer by *ca.* 15 pm for Pd than for Ni, according to the different size of each metal centre (see above).[18] Despite the elongated metal–ligand distances in **6′**, the corresponding cell volume (1.48999(14) nm^3) is comparable to that of the isomorphous Ni compound (1.5044(6) nm^3). Thus, the fine structural differences in the metal coordination environments do not have any significant effect in the interionic separation. The Pd–C(aryl) distances are slightly longer in **6′** (202.8(4) pm average value) than in **1** (196.9(4) pm average value), probably due to the anionic nature of the former. The Pd–Br distance (248.21(5) pm) compares well with the mean value derived from a number of four-coordinate compounds with terminal Pd–Br bonds (245.0 pm).[16] On the other hand, the Pd–CO distance (196.1(4) pm) is longer than usually found in terminal carbonyl derivatives of Pd^{II} as will be commented later on.

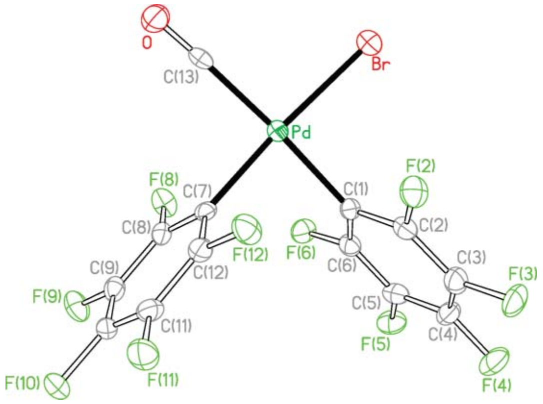

Fig. 4 Thermal ellipsoid diagram (50% probability) of the $[\textit{cis}\text{-}Pd(C_6F_5)_2Br(CO)]^-$ anion in **6′**. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Pd–C(1) 202.4(4), Pd–C(7) 203.2(4), Pd–C(13) 196.1(4), Pd–Br 248.21(5), C(1)–C(2) 137.8(5), C(1)–C(6) 137.9(5), C(13)–O 110.4(4), C(7)–C(8) 137.0(5), C(7)–C(12) 137.0(5), C(1)–Pd–C(7) 86.27(13), C(1)–Pd–C(13) 176.23(14), C(1)–Pd–Br 89.56(10), C(7)–Pd–C(13) 90.18(14), C(7)–Pd–Br 175.83(10), C(13)–Pd–Br 93.99(10), Pd–C(1)–C(2) 123.3(3), Pd–C(1)–C(6) 121.8(3), C(2)–C(1)–C(6) 114.9(3), Pd–C(7)–C(12) 121.8(3), Pd–C(7)–C(8) 122.4(3), C(8)–C(7)–C(12) 115.8(3), Pd–C(13)–O 177.9(3).

Synthesis and characterization of $[NBu_4][\{Pd(C_6F_5)_2(CO)\}_2(\mu\text{-}Cl)]$ (11)

We sought to exploit the residual nucleophilicity of the halocarbonyl derivatives of Pd^{II} in a productive way. For this purpose, we reacted $[NBu_4][\textit{cis}\text{-}Pd(C_6F_5)_2Cl(CO)]$ (**5**) with the dicarbonyl

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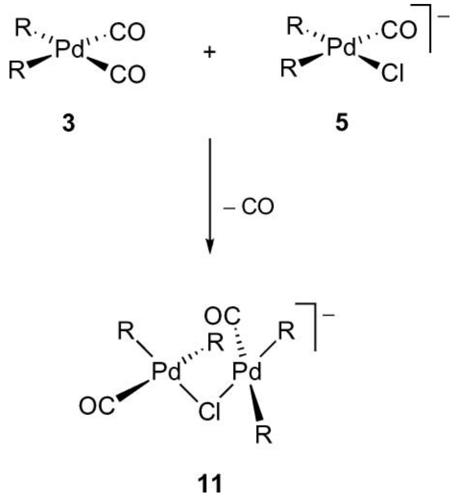
§ Although two IR-active X-sensitive absorptions would also be expected for the *trans* isomers, their experimental relative intensities are usually so different that one of them is barely observable, if at all.[28]

derivative *cis*-[Pd(C_6F_5)$_2$(CO)$_2$] (**3**), a process resulting in the formation of the dinuclear compound [NBu$_4$][{Pd(C_6F_5)$_2$(CO)}$_2$(μ-Cl)] (**11**) in good yield (Scheme 2). In this reaction, the anion [*cis*-Pd(C_6F_5)$_2$Cl(CO)]$^-$ of **5** acts as a metalloligand towards neutral complex **3**, in which it causes the replacement of one of the CO ligands.



Scheme 2 Synthesis of the dinuclear carbonyl-palladium(II) derivative **11** (R = C_6F_5) isolated as its [NBu$_4$]$^+$ salt.

Compound **11** is stable enough to allow its isolation and characterization by X-ray diffraction methods. A drawing of the dinuclear anion [{Pd(C_6F_5)$_2$(CO)}$_2$(μ-Cl)]$^-$ as found in single crystals of **11** is given in Fig. 5. It consists of two Pd atoms, each in an approximately *SP*-4 environment, connected by a single bridging chloro ligand. The coordination planes of the two Pd atoms form a dihedral angle of 76.3°. The Pd(1)–Cl–Pd(2) bridging unit forms almost a right angle: 91.21(3)°, which is a suitable geometry to enable the μ-Cl atom to make optimal use of its p orbitals.[29] The intramolecular Pd(1) · · · Pd(2) separation (344.5 pm) is too long to denote the existence of any metal–metal bonding interaction. The two Pd(C_6F_5)$_2$(CO) units adopt a mutual *transoidal* disposition so that intramolecular non-bonded repulsions are minimized. The C_6F_5 groups are tilted and form dihedral angles in the range 63.4–73.0° with the corresponding metal coordination plane. The Pd–Cl distances are indistinguishable and compare well with those found in four-coordinate Pd^{II} compounds containing bridging Cl ligands (mean value: 240.4 pm).[16] All four Pt–C(aryl) distances are also virtually identical and do not appreciably deviate from those found in the mononuclear halocarbonyl derivative **6′** (see above). The Pd–CO distances in **11** (198.3(5) pm) are similar to that observed in **6′** (196.1(4) pm) and longer than those usually found in other structurally characterized four-coordinate Pd^{II} derivatives containing terminal carbonyl groups. Even in the cationic and highly electrophilic tetracarbonyl derivative [Pd(CO)$_4$][Sb$_2$F$_{11}$]$_2$ the Pd–CO distances (mean value: 199.2(6) pm) are comparable with those found in **11**.[8]

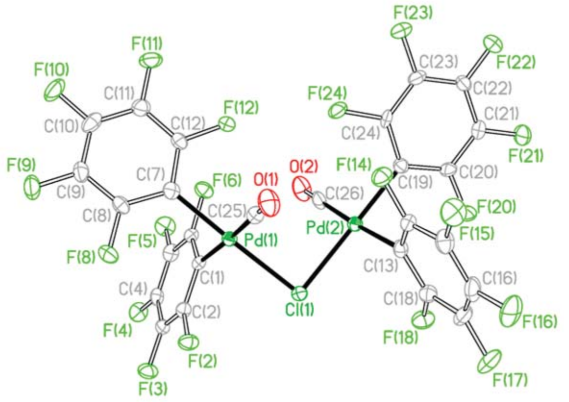


Fig. 5 Structural drawing (with 50% probability thermal ellipsoids for the heavy atoms) of the dinuclear [{Pd(C_6F_5)$_2$(CO)}$_2$(μ-Cl)]$^-$ anion in **11**·CH$_2$Cl$_2$. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Pd(1)–C(1) 202.7(4), Pd(1)–C(7) 201.0(4), Pd(1)–C(25) 198.3(5), Pd(1)–Cl(1) 240.9(1), Pd(2)–C(13) 202.4(4), Pd(2)–C(19) 201.5(4), Pd(2)–C(26) 198.2(5), Pd(2)–Cl(1) 241.2(1), C(25)–O(1) 112.1(5), C(26)–O(2) 112.2(5), C(1)–Pd(1)–C(7) 84.3(2), C(1)–Pd(1)–C(25) 174.0(2), C(1)–Pd(1)–Cl(1) 91.7(1), C(7)–Pd(1)–C(25) 92.6(2), C(7)–Pd(1)–Cl(1) 173.5(1), C(25)–Pd(1)–Cl(1) 92.2(1), Pd(1)–C(25)–O(1) 175.5(4), Pd(1)–Cl(1)–Pd(2) 91.21(3), C(13)–Pd(2)–C(19) 85.5(2), C(13)–Pd(2)–C(26) 175.1(2), C(13)–Pd(2)–Cl(1) 91.8(1), C(19)–Pd(2)–C(26) 90.9(2), C(19)–Pd(2)–Cl(1) 176.2(1), C(26)–Pd(2)–Cl(1) 91.9(1), Pd(2)–C(26)–O(2) 176.5(4).

The presence of two chemically inequivalent types of C_6F_5 groups in the ^{19}F NMR spectrum of **11** in solution is in keeping with the solid state structure just described. The IR spectrum of **11** in CH$_2$Cl$_2$ solution shows a single, sharp ν(CO) absorption at 2134 cm^{-1}. The increase of 10 cm^{-1} with respect to the value observed in the mononuclear parent compound **5** (Table 1) evidences the lowered donor ability of the bridging *vs.* terminal Cl ligand.

Dinuclear d^8 metal compounds with bridging halo ligands usually adopt a doubly bridging M(μ-X)$_2$M′ pattern.[30] Homo- or hetero-dimetallic compounds containing a single bridging halo core M(μ-X)M′ are far less common. These kinds of compounds are of interest because of their mechanistic implications. They act as formal models for the synthetically useful process taking place under splitting of the doubly bridging M(μ-X)$_2$M′ system, as well as for the reverse reaction. They have also been found to be involved in halide abstraction processes.[31] Compound **11** is of particular relevance in the reaction leading to the mononuclear derivatives **5–10**, and also in the counter-reaction causing their decomposition (Scheme 1). Most of the structurally characterized precedents of d^8 metal compounds with unsupported single bridging halo ligands contain additional polydentate or π-coordinated ligands, that probably contribute to their stabilization.[32] As far as we know, the only previous case with just monodentate ligands is [{*trans*-PtH(P^{i}Pr$_3$)$_2$}$_2$(μ-I)][B{C$_6$H$_3$(CF$_3$)$_2$-3,5}$_4$],[33] for which a very wide Pt–I–Pt angle was observed: 170.14(9)°.

Concluding remarks

Dicarbonyl-palladium(II) compounds with formula *cis*-[PdR$_2$(CO)$_2$] [R = C_6F_5 (**3**), C_6Cl_5 (**4**)] have been prepared in good yield by replacing the labile thf ligands in the solvento-complexes *cis*-[PdR$_2$(thf)$_2$] [R = C_6F_5 (**1**), C_6Cl_5 (**2**)] by CO under mild conditions. Isolation of these compounds has been possible, among other reasons, because of the small residual nucleophilicity of the metal-bound perhalophenyl groups, together with the reluctance of the M–R bonds to undergo CO insertion. The high frequency values observed for the IR-active ν(CO) vibration modes in compounds **3** and **4** are to be attributed to the marked electron-withdrawing character of the R groups. According to the IR data (Table 1), the electron-withdrawing ability of the C_6F_5 group is even greater than that of the C_6Cl_5 one.

Splitting of the double-bridging system in the dinuclear compounds $[NBu_4]_2[\{PdR_2\}_2(\mu\text{-}X)_2]$ (X = Cl, Br, I) by CO leads to the formation of the monocarbonyl-palladium(II) compounds [NBu$_4$][*cis*-PdR$_2$X(CO)] (**5–10**) in solution. With the synthesis of these Pd compounds, we have completed a family of homologous compounds of formula [*cis*-MR$_2$X(CO)]$^-$ for all three Group 10 metals (M = Ni, Pd, Pt). We have found that the ν(CO) frequency values are higher for Pd than for Ni or Pt. The ν(CO) values also depend upon the *cis* influence of the halo ligands, following the decreasing order of electronegativity: Cl > Br > I. The range of stability of the monocarbonyl derivatives of Ni and Pd is rather limited because of the considerable residual nucleophilicity of the metal-bound halo ligands, M–X. The readiness of these compounds to extrude CO following an intermolecular substitution process, which is the reverse of the procedure leading to their synthesis (Scheme 1), hinders their isolation. Thus, we did not managed to isolate compound **7** (R = C_6F_5; X = I). The higher stability of the corresponding Pt compounds is probably due to a combination of thermodynamic (intrinsically more stable Pt–CO bonds) and kinetic (slower decomposition reaction rates) reasons.

The residual nucleophilicity of the Pd-bound Cl atom at the [*cis*-Pd(C_6F_5)$_2$Cl(CO)]$^-$ anion enables this unit to act as a metalloligand towards the dicarbonyl derivative **3** affording $[NBu_4][\{Pd(C_6F_5)_2(CO)\}_2(\mu\text{-}Cl)]$ (**11**) in reasonable yield. This dinuclear derivative consists of two symmetric *SP*-4 units sharing a vertex. The Pd–Cl–Pd angle [91.21(3)°] closely approaches a right angle, which is considered to be the most appropriate geometry to enable an optimal use of the p orbitals on the single bridging halo ligand. Compound **11** can be taken as a model of the intermediate species presumably involved in the splitting of the double bridging halide system in complexes $[NBu_4]_2[\{PdR_2\}_2(\mu\text{-}X)_2]$ by CO (Scheme 1).

No *cis*/*trans* isomerization has been observed in any of the processes reported in this paper that take place with stereoretention.

Experimental

General procedures and materials

Unless otherwise stated, the reactions and manipulations were carried out under purified argon using Schlenk techniques. Solvents were dried using an MBraun SPS-800 System. Compounds $[NBu_4]_2[\{Pd(C_6F_5)_2\}_2(\mu\text{-}X)_2]$ (X = Cl, Br, I)[34] and $[NBu_4]_2[\{Pd(C_6Cl_5)_2\}_2(\mu\text{-}X)_2]$ (X = Cl, Br, I)[35] were obtained following the appropriate published methods. Elemental analyses were carried out with a Perkin-Elmer 2400-Series II microanalyzer. IR spectra of CH_2Cl_2 solution samples, Nujol mulls or KBr discs were recorded on a Perkin-Elmer 883 spectrophotometer (4000–200 cm^{-1}). NMR spectra were recorded on any of the following spectrometers: Varian Unity-300, Bruker ARX 300 or Bruker ARX 400. Unless otherwise stated, the spectroscopic measurements were carried out at room temperature.

Synthesis of *cis*-[Pd(C_6F_5)$_2$(thf)$_2$] (1)

Compound **1** was prepared following a previously reported method.[19e] Elemental analysis calcd (%) for $C_{20}H_{16}F_{10}O_2Pd$: C 41.1, H 2.7; found: C 40.8, H 2.9. IR (Nujol): $\tilde{\nu}_{max}$ 1638 (m), 1603 (w), 1496 (s), 1362 (m), 1355 (m), 1256 (w), 1058 (s), 1037 (s), 954 (vs; ν_{CF}), 884 (vs; thf: C–O–C),[37] 802 (s; C_6F_5: X-sensitive vibr.),[36] 792 cm^{-1} (s; C_6F_5: X-sensitive vibr.).[36] ^{1}H NMR ([^{2}H]-chloroform): δ 3.79 (4H, α-CH$_2$), 1.82 (4H, β-CH$_2$) ppm. ^{19}F NMR ([^{2}H]-chloroform): δ −117.3 (4F, *o*-F), −159.8 (2F, *p*-F), −163.4 (4F, *m*-F) ppm.

Single crystals of **1** suitable for X-ray diffraction purposes were obtained by slow diffusion of an *n*-hexane (5 cm^3) layer into a solution of 30 mg of **1** in 2 cm^3 of CH_2Cl_2 at −30 °C.

Synthesis of *cis*-[Pd(C_6Cl_5)$_2$(thf)$_2$] (2)

Compound **2** was prepared following a previously reported method.[19e] Elemental analysis calcd (%) for $C_{20}H_{16}Cl_{10}O_2Pd$: C 32.05, H 2.1; found: C 31.7, H 2.6. IR (Nujol): $\tilde{\nu}_{max}$ 1334 (s), 1313 (s), 1289 (s), 1260 (m), 1208 (m), 1150 (m), 1088 (m), 1046 (s), 1028 (s), 1003 (m), 875 (s; thf: C–O–C),[37] 841 (s; C_6Cl_5: X-sensitive vibr.),[36] 832 (s; C_6Cl_5: X-sensitive vibr.),[36] 788 (m), 673 (vs), 627 (m; $\nu_{Pt\text{-}C}$),[38] 617 cm^{-1} (m; $\nu_{Pt\text{-}C}$).[38] ^{1}H NMR ([^{2}H]-dichloromethane): δ 3.72 (4H, α-CH$_2$), 1.78 (4H, β-CH$_2$) ppm.

Synthesis of *cis*-[Pd(C_6F_5)$_2$(CO)$_2$] (3)

A CH_2Cl_2 (10 cm^3) solution of **1** (0.19 g, 0.32 mmol) at −78 °C was allowed to react for 30 min with CO at atmospheric pressure, whereupon a white solid started to form. Addition of *n*-hexane (30 cm^3) at −78 °C caused the precipitation of a larger amount of white solid, which was filtered at −78 °C and vacuum-dried at −40 °C (**3**: 0.14 g, 0.29 mmol, 90% yield). Due to its high instability, no satisfactory elemental analyses could be obtained for **3**. IR (Nujol): $\tilde{\nu}_{max}$ 2186 (vs; ν_{CO}), 2163 (vs; ν_{CO}), 1640 (m), 1610 (w), 1511 (vs), 1084 (s), 1067 (s), 962 (vs; ν_{CF}), 798 (s; C_6F_5: X-sensitive vibr.),[36] 786 (s; C_6F_5: X-sensitive vibr.),[36] 448 (m), 422 (m), 382 (w), 330 cm^{-1} (w). ^{19}F NMR ([^{2}H]-chloroform, −50 °C): δ −116.3 (4F, *o*-F), −155.4 (2F, *p*-F), −160.8 (4F, *m*-F) ppm.

Synthesis of *cis*-[Pd(C_6Cl_5)$_2$(CO)$_2$] (4)

Compound **4** was prepared from **2** (0.27 g, 0.36 mmol) by using a similar procedure to that just described for the synthesis of **3**. Complex **4** was obtained as a white solid (0.13 g, 0.20 mmol, 56% yield). Elemental analysis calcd (%) for $C_{14}Cl_{10}O_2Pd$: C 25.4; found: C 25.1. IR (Nujol): $\tilde{\nu}_{max}$ 2173 (vs; ν_{CO}), 2152 (vs; ν_{CO}), 1327 (vs), 1321 (vs), 1295 (vs), 840 (sh; C_6Cl_5: X-sensitive vibr.),[36] 833 (s; C_6Cl_5: X-sensitive vibr.),[36] 670 (vs), 619 (sh; $\nu_{Pt\text{-}C}$),[38] 614 (s; $\nu_{Pt\text{-}C}$),[38] 482 (s), 444 (m), 412 (m), 384 (w), 370 (w), 339 (w), 323 cm^{-1} (w).

Synthesis of [NBu$_4$][*cis*-Pd(C_6F_5)$_2$Cl(CO)] (5)

A solution of $[NBu_4]_2[\{Pd(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]$ (0.201 g, 0.140 mmol) in CH_2Cl_2 (8 cm^3) at 0 °C was allowed to react with CO. The colour of the solution gradually faded. After 1 h of stirring, the solution was cooled to −78 °C and CO-saturated *n*-hexane (15 cm^3) was added, causing the precipitation of a white solid, which was filtered at −78 °C and dried at the same temperature in an Ar stream (**5**: 0.181 g, 0.243 mmol, 87% yield). Elemental analysis calcd (%) for

$C_{29}H_{36}ClF_{10}NOPd$: C 46.7, H 4.9, N 1.9; found: C 47.1, H 5.3, N 2.0. IR (KBr): $\tilde{\nu}_{max}$ 2967 (s), 2878 (s), 2114 (vs; ν_{CO}), 1498 (vs), 1459 (vs), 1380 (w), 1360 (m), 1055 (s), 955 (vs; ν_{CF}), 881 (m; $[NBu_4]^+$), 795 (s; C_6F_5: X-sensitive vibr.),[36] 781 (s; C_6F_5: X-sensitive vibr.),[36] 739 cm^{-1} (m). ^{19}F NMR ([^{2}H]-chloroform, −20 °C): δ −115.7 (2F, *o*-F), −116.2 (2F, *o*-F), −160.4 (1F, *p*-F), −161.7 (1F, *p*-F), −163.6 (2F, *m*-F), −164.1 (2F, *m*-F) ppm.

Synthesis of $[NBu_4][cis\text{-}Pd(C_6F_5)_2Br(CO)]$ (6)

Compound **6** was prepared from $[NBu_4]_2[\{Pd(C_6F_5)_2\}_2(\mu\text{-}Br)_2]$ (0.163 g, 0.107 mmol) by using the procedure described for the synthesis of **5**. Complex **6** was obtained as a white solid (0.127 g, 0.161 mmol, 75% yield). Elemental analysis calcd (%) for $C_{29}H_{36}BrF_{10}NOPd$: C 44.0, H 4.6, N 1.8; found: C 43.9, H 4.5, N 1.8. IR (KBr): $\tilde{\nu}_{max}$ 2968 (s), 2880 (s), 2113 (vs; ν_{CO}), 1497 (vs), 1458 (vs), 1381 (w), 1361 (m), 1056 (s), 956 (vs; ν_{CF}), 881 (m; $[NBu_4]^+$), 794 (s; C_6F_5: X-sensitive vibr.),[36] 780 (s; C_6F_5: X-sensitive vibr.),[36] 738 cm^{-1} (m). ^{19}F NMR ([^{2}H]-chloroform, −20 °C): δ −115.6 (2F, *o*-F), −115.8 (2F, *o*-F), −160.3 (1F, *p*-F), −161.8 (1F, *p*-F), −163.4 (2F, *m*-F), −164.2 (2F, *m*-F) ppm.

Spectroscopic detection of $[NBu_4][cis\text{-}Pd(C_6F_5)_2I(CO)]$ (7)

The synthesis of **7** was attempted starting from $[NBu_4]_2[\{Pd(C_6F_5)_2\}_2(\mu\text{-}I)_2]$ (0.108 g, 0.067 mmol) using the procedure described for the synthesis of **5**. Although compound **7** was observed to form in solution by IR (Table 1) and ^{19}F NMR spectroscopies, our attempts to isolate it rendered *ca.* 75% of the dinuclear starting material. ^{19}F NMR ([^{2}H]-chloroform, −20 °C): δ −114.3 (2F, *o*-F), −116.3 (2F, *o*-F), −160.3 (1F, *p*-F), −162.0 (1F, *p*-F), −163.3 (2F, *m*-F), −164.4 (2F, *m*-F) ppm.

Synthesis of $[NBu_4][cis\text{-}Pd(C_6Cl_5)_2Cl(CO)]$ (8)

Compound **8** was prepared from $[NBu_4]_2[\{Pd(C_6Cl_5)_2\}_2(\mu\text{-}Cl)_2]$ (0.065 g, 0.037 mmol) using the procedure described for the synthesis of **5**. Complex **8** was obtained as a white solid (0.033 g, 0.036 mmol, 50% yield). Elemental analysis calcd (%) for $C_{29}H_{36}Cl_{11}NOPd$: C 38.2, H 4.0, N 1.6; found: C 37.8, H 4.2, N 1.5. IR (KBr): $\tilde{\nu}_{max}$ 2962 (s), 2875 (s), 2113 (vs; ν_{CO}), 1472 (s), 1381 (m), 1327 (vs), 1316 (vs), 1289 (vs), 1221 (m), 1155 (w), 881 (m; $[NBu_4]^+$), 837 (m; C_6Cl_5: X-sensitive vibr.),[36] 738 (m), 673 (vs), 611 (s; $\nu_{Pt\text{-}C}$),[38] 458 cm^{-1} (m).

Synthesis of $[NBu_4][cis\text{-}Pd(C_6Cl_5)_2Br(CO)]$ (9)

Compound **9** was prepared from $[NBu_4]_2[\{Pd(C_6Cl_5)_2\}_2(\mu\text{-}Br)_2]$ (0.068 g, 0.036 mmol) using the procedure described for the synthesis of **5**. Complex **9** was obtained as a white solid (0.032 g, 0.033 mmol, 46% yield). Elemental analysis calcd (%) for $C_{29}H_{36}BrCl_{10}NOPd$: C 36.4, H 3.8, N 1.5; found: C 36.2, H 3.7, N 1.3. IR (KBr): $\tilde{\nu}_{max}$ 2962 (s), 2874 (s), 2109 (vs; ν_{CO}), 1480 (s), 1379 (m), 1327 (vs), 1316 (vs), 1288 (vs), 1221 (m), 1150 (w), 881 (m; $[NBu_4]^+$), 835 (m; C_6Cl_5: X-sensitive vibr.),[36] 738 (m), 673 (vs), 609 (s; $\nu_{Pt\text{-}C}$),[38] 457 cm^{-1} (m).

Synthesis of $[NBu_4][cis\text{-}Pd(C_6Cl_5)_2I(CO)]$ (10)

Compound **10** was prepared from $[NBu_4]_2[\{Pd(C_6Cl_5)_2\}_2(\mu\text{-}I)_2]$ (0.102 g, 0.052 mmol) by using the procedure described for the synthesis of **5**. Complex **10** was obtained as a white solid (0.059 g, 0.059 mmol, 57% yield). Elemental analysis calcd (%) for $C_{29}H_{36}Cl_{10}INOPd$: C 34.7, H 3.6, N 1.4; found: C 34.9, H 3.8, N 1.6. IR (KBr): $\tilde{\nu}_{max}$ 2963 (s), 2875 (s), 2104 (vs; ν_{CO}), 1479 (s), 1380 (m), 1313 (vs), 1283 (vs), 1219 (m), 1151 (w), 881 (m; $[NBu_4]^+$), 816 (w; C_6Cl_5: X-sensitive vibr.),[36] 739 (m), 669 (vs), 614 (s; $\nu_{Pt\text{-}C}$),[38] 582 cm^{-1} (m).

Synthesis of $[NBu_4][\{Pd(C_6F_5)_2(CO)\}_2(\mu\text{-}Cl)]$ (11)

A CH_2Cl_2 solution (10 cm^3) of **5** was prepared from $[NBu_4]_2[\{Pd(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]$ (0.14 g, 0.10 mmol) as described above and was cooled to −40 °C. To this solution generated *in situ* was added **3** (0.10 g, 0.20 mmol) dissolved in CH_2Cl_2 at the same temperature and the mixture was allowed to slowly warm to 0 °C, while several vacuum/Ar cycles were applied. Then *n*-hexane (40 cm^3) was overlaid. After standing at −30 °C overnight, a white solid formed which was filtered at −40 °C and vacuum dried (**11**: 0.12 g, 0.10 mmol, 50% yield). Elemental analysis calcd (%) for $C_{42}H_{36}ClF_{20}NO_2Pd_2$: C 41.5, H 3.0, N 1.1; found: C 41.4, H 3.0, N 1.1. IR (KBr): $\tilde{\nu}_{max}$ 2145 (vs; ν_{CO}), 1504 (vs), 1464 (vs), 1361 (m), 1059 (s), 959 (vs; ν_{CF}), 880 (w; $[NBu_4]^+$), 798 (s; C_6F_5: X-sensitive vibr.),[36] 789 cm^{-1} (s; C_6F_5: X-sensitive vibr.).[36] ^{19}F NMR ([^{2}H]-dichloromethane, −80 °C): δ −116.1 (2F, *o*-F), −117.1 (2F, *o*-F), −159.6 (1F, *p*-F), −160.1 (1F, *p*-F), −163.2 (2F, *m*-F), −163.5 (2F, *m*-F) ppm.

Single crystals of **11** suitable for X-ray diffraction purposes were obtained by slow diffusion of an *n*-hexane (8 cm^3) layer into a solution of 40 mg of **11** in 2 cm^3 of CH_2Cl_2 at −30 °C.

Single crystals of $cis\text{-}[Pt(C_6Cl_5)_2(CO)_2]\cdot 3H_2O$

Single crystals suitable for X-ray diffraction purposes with formula $cis\text{-}[Pt(C_6Cl_5)_2(CO)_2]\cdot 3H_2O$ were obtained by slow diffusion of an *n*-hexane (5 cm^3) layer into a solution of $cis\text{-}[Pt(C_6Cl_5)_2(CO)_2]$[28] (30 mg) in CH_2Cl_2 (2 cm^3) at −30 °C.

X-Ray structure determinations†

Crystal data and other details of the structure analysis are presented in Table 2. Crystals were mounted on quartz fibres in a random orientation and held in place with fluorinated oil. Graphite monochromated Mo-Kα radiation ($\lambda = 71.073$ pm) was used in all cases. For **1** and **6′** diffraction data were collected on a Bruker Smart Apex CCD diffractometer, and the diffraction frames were integrated using the SAINT package[39] and corrected for absorption with SADABS.[40] For $cis\text{-}[Pt(C_6Cl_5)_2(CO)_2]\cdot 3H_2O$, data collection was performed on a Enraf Nonius CAD4 diffractometer, and an absorption correction was applied based on 310 azimuthal scan data. For $\mathbf{11}\cdot CH_2Cl_2$, data collection was performed on a Oxford Diffraction Xcalibur CCD diffractometer, and the diffraction frames were integrated and corrected for absorption using the CrysAlis RED package.[41] Lorentz and polarisation corrections were applied for all the structures.

The structures were solved by Patterson and direct methods. All non-hydrogen atoms of the complexes were assigned anisotropic displacement parameters. For $cis\text{-}[Pt(C_6Cl_5)_2(CO)_2]\cdot 3H_2O$, the hydrogen atoms were not located in the density map and were not included in the refinement. For the remaining structures, the hydrogen atoms were constrained to idealised geometries

Table 2 Crystal data and structure refinement for complexes **1**, *cis*-[Pt(C_6Cl_5)$_2$(CO)$_2$]·3H_2O, **6′** and **11**·CH_2Cl_2

	1	*cis*-[Pt(C_6Cl_5)$_2$(CO)$_2$]·3H_2O	**6′**	**11**·CH_2Cl_2
Formula	$C_{20}H_{16}F_{10}O_2Pd$	$C_{14}Cl_{10}O_2Pt\cdot 3H_2O$	$C_{32}H_{18}BrF_{10}OPPd$	$C_{42}H_{36}ClF_{20}NO_2Pd_2\cdot CH_2Cl_2$
FW	584.73	803.78	825.74	1299.89
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$Pbca$
a/pm	928.30(6)	2020.6(2)	1107.37(6)	1812.82(5)
b/pm	956.52(6)	1251.90(15)	1143.35(6)	1825.09(8)
c/pm	1279.16(8)	1182.45(13)	1395.72(8)	2960.36(8)
α/°	69.777(1)	90	113.680(1)	90
β/°	74.253(1)	122.90(1)	107.883(1)	90
γ/°	83.994(1)	90	95.584(1)	90
V/nm^3	1.02572(11)	2.5114(5)	1.48999(14)	9.7945(6)
Z	2	4	2	8
D_c/g cm^{-3}	1.893	2.126	1.841	1.763
T/K	100(2)	293(2)	100(2)	100(1)
μ/mm^{-1}	1.010	6.675	2.107	1.012
F(000)	576	1512	808	5136
θ range/°	1.75–23.29	3.44–24.99	1.72–23.29	4.52–25.06
Collected reflections	6830	1844	9935	27 465
Unique reflections	2960	1844	4297	8559
R_{int}	0.0279	0	0.0196	0.0320
$R_1{}^a$, w$R_2{}^b$ ($I > 2\sigma(I)$)	0.0398, 0.1061	0.0348, 0.0913	0.0285, 0.0738	0.0442, 0.1043
$R_1{}^a$, $wR_2{}^b$(all data)	0.0428, 0.1079	0.0370, 0.0929	0.0339, 0.0754	0.0554, 0.1100
Max, min $\Delta\rho$/e nm^{-3}	1583, −1051	972, −851	481, −513	1186, −911
GOF (F^2)^c	1.006	1.092	1.020	1.091

^{a} $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$. ^{c} Goodness-of-fit $=[\sum w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

and assigned isotropic displacement parameters equal to 1.2 or 1.5 times the U_{iso} values of their respective parent atoms. Full-matrix least-squares refinement of these models against F^2 using the SHELXL-93[42] (*cis*-[Pt(C_6Cl_5)$_2$(CO)$_2$]·3H_2O) or SHELXL-97[43] (**1**, **6′** and **11**·CH_2Cl_2) programs converged to final residual indices given in Table 2.

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