Enthalpy of ligand substitution in *cis* organopalladium complexes with monodentate ligands†

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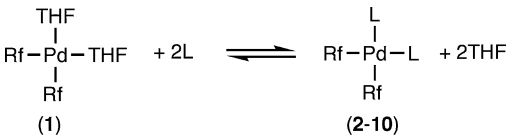
The enthalpy for the substitution reaction *cis*-[PdRf$_2$(THF)$_2$] + 2 L → *cis*-[PdRf$_2$L$_2$] + 2THF (THF = tetrahydrofuran) has been measured in THF by calorimetric methods for Rf = 3,5-dichloro-2,4,6-trifluorophenyl, L = PPh_3, $AsPh_3$, $SbPh_3$, $PMePh_2$, $PCyPh_2$, PMe_3, $AsMePh_2$, or L_2 = dppe (1,2-bis(diphenylphosphino)ethane), dppf (1,1′-bis(diphenylphosphino)ferrocene). The values determined show that the substitution enthalpy has a strong dependence on the electronic and steric properties of the ligand. The study of the consecutive substitution reactions *cis*-[PdRf$_2$(THF)$_2$] + L → *cis*-[PdRf$_2$L(THF)] + THF, and *cis*-[PdRf$_2$L(THF)] + L → *cis*-[PdRf$_2$L$_2$] + THF has been carried our for L = PPh_3 and L = $PCyPh_2$. The first substitution is clearly more favorable for the bulkier leaving ligand, but the second gives practically the same ΔH value for both cases, indicating that the differences in steric hindrance happen to compensate the electronic differences for both ligands. The X-ray structures of *cis*-[PdRf$_2$($PMePh_2$)$_2$], *cis*-[PdRf$_2$(dppe)] and *cis*-[PdRf$_2$(dppf)] are reported.

Introduction

The success of a metal-catalyzed cycle often depends on the ease of ligand dissociation or ligand substitution in steps involving isomerization, insertion, or reductive elimination. Thus, ligand dissociation or ligand substitution enthalpy data are interesting to estimate the feasibility of a process, or to understand the catalytic activity observed. For organometallic compounds there are direct calorimetric determinations on Fe,[1] Cr and W,[2] Ni,[3] Mo,[4] Ru,[5] Rh,[4c,5l,6] Os,[7] and Pt[8] complexes. Surprisingly, although palladium complexes, often bearing phosphines or arsines as ancillary ligands (L), are among the most versatile and useful catalysts in organic synthesis,[9] the only data available for Pd refer to the substitution of benzonitrile in [PdCl$_2$(C_6H_5CN)$_2$] by PPh_3 and by dppe (dppe = 1,2-bis(diphenylphosphino)ethane).[10] No data are available for ligand dissociation or ligand substitution enthalpy in Pd organometallics.

In this work we present a calorimetric study of the substitution of THF, in the aryl complex *cis*-[PdRf$_2$(THF)$_2$] (**1**) (Rf = 3,5-dichloro-2,4,6-trifluorophenyl; THF = tetrahydrofuran), by ligands often used in homogeneous catalysis (PPh_3, $PMePh_2$, $PCyPh_2$, PMe_3, dppe (1,2-bis(diphenylphosphino)ethane), dppf (1,1′-bis(diphenylphosphino)ferrocene, $AsPh_3$, $AsMePh_2$, and $SbPh_3$) (Scheme 1). Complex **1** was chosen as a model of the type of intermediate from which reductive elimination takes place, either directly *via* L substitution or *via* L dissociation, because of the remarkable stability of the fluoroaryl palladium(II) derivatives. In fact this complex does not undergo reductive elimination during the calorimetric study and the measurement of L substitutions is not interfered by competitive coupling. Moreover, the reaction products are easily characterized by ^{19}F NMR.[11,12,13] Finally, THF is such a weak ligand for Pd that substitution can be measured even with weak ligands such as arsines and stibines.



L = PPh_3 (**2**), $PCyPh_2$ (**3**), $PMePh_2$ (**4**), PMe_3 (**5**)

2 L = dppe (**6**), dppf (**7**)

L = $AsPh_3$ (**8**), $AsMePh_2$ (**9**), $SbPh_3$ (**10**)

Scheme 1

Results and discussion

For preparative purposes [PdRf$_2$(COD)] (COD = 1,5-cyclooctadiene), more stable and easier to store and handle than **1**, was used to prepare complexes **2–10** by substitution of COD in THF solution. The new compounds **3**, **4**, and **6–10** were fully characterized by elemental analysis and spectroscopic methods. The spectroscopic data of the complexes were used for their identification in solution. Crystals suitable for X-ray diffraction were obtained for **4**, **6** and **7** (see Fig. 1 for ORTEP diagrams, and Table 1 for selected data) and confirmed that the three complexes are mononuclear *cis* isomers. Full crystallographic data are given in the ESI (Tables SI4, SI5 and S16).†

Complex **4** crystallizes in the $P\bar{1}$ group with one molecule in the asymmetric unit. The Pd–C lengths and C–Pd–C angle are very similar to those reported for *cis*-[Pd(C_6F_5)$_2$(PPh_3)$_2$] (2.053(6) Å, 2.060(6) Å and 84.7(3)°).[14] The P–Pd lengths and P–Pd–P and C–Pd–C angles are also close to those found in other complexes with two *cis* PPh_2Me ligands.[15,16] Complex **6** crystallizes in the $P2_1/n$ group, with one molecule in the asymmetric unit. The

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Table 1 Selected bond lengths and angles for complexes **4**, **6** and **7**

Bond lengths/Å		Bond angles/°	
cis-[PdRf$_2$(PMePh$_2$)$_2$] (**4**)			
Pd(1)–C(1)	2.048(3)	C(1)–Pd(1)–C(7)	84.98(10)
Pd(1)–C(7)	2.060(2)	C(7)–Pd(1)–P(1)	90.16(7)
Pd(1)–P(1)	2.3282(9)	C(1)–Pd(1)–P(2)	89.44(7)
Pd(1)–P(2)	2.3317(9)	P(1)–Pd(1)–P(2)	95.48(3)
[PdRf$_2$(dppe)] (**6**)			
Pd(1)–C(1)	2.016(9)	C(1)–Pd(1)–C(7)	87.8(3)
Pd(1)–C(7)	2.057(8)	C(1)–Pd(1)–P(1)	91.4(2)
Pd(1)–P(1)	2.304(2)	C(7)–Pd(1)–P(2)	96.4(2)
Pd(1)–P(2)	2.323(2)	P(1)–Pd(1)–P(2)	84.72(8)
[PdRf$_2$(dppf)] (**7**)			
Pd(1)–C(1)	2.058(2)	C(1)–Pd(1)–C(7)	85.20(9)
Pd(1)–C(7)	2.066(2)	C(1)–Pd(1)–P(1)	88.41(6)
Pd(1)–P(1)	2.3397(8)	C(7)–Pd(1)–P(2)	87.16(7)
Pd(1)–P(2)	2.3685(9)	P(1)–Pd(1)–P(2)	99.07(2)

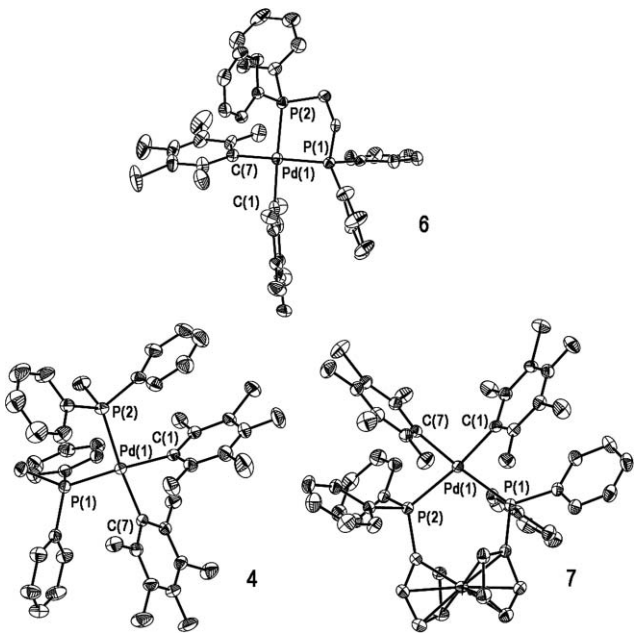


Fig. 1 ORTEP diagram of the complexes *cis*-[PdRf$_2$(PMePh$_2$)$_2$] (**4**), [PdRf$_2$(dppe)] (**6**), and [PdRf$_2$(dppf)] (**7**). H atoms have been omitted for clarity.

Pd–C and Pd–P lengths are similar to the reported values for other palladium complexes with dppe,[17,18,19,20] with two *cis* PMePh$_2$ ligands. It is also very common that the P–Pd–P angles are larger for complexes with two PMePh$_2$ ligands than with dppe, while the contrary holds for the C–Pd–C angle.

Complex **7** crystallizes in the $P2_1/n$ group, with one molecule in the asymmetric unit. The Pd–C and Pd–P lengths found in [PdRf$_2$(dppf)] are close to the values reported in the two structures of *cis*-organometallic complexes with a Pd(dppf) moiety and two Pd–C bonds have been previously reported,[21] while the P–Pd–P angle is in between the two values reported.

A comparison of the Pd–P lengths reported for *cis*-[PdCl$_2$(PMePh$_2$)$_2$] (2.267(2), 2.262(2) Å), [PdCl$_2$(dppe)] (2.264(3), 2.284(3) Å), and [PdCl$_2$(dppf)] (2.301(1), 2.283(1) Å), with those found for **4**, **6**, and **7** (Table 1) shows that the *trans* influence of the aryl ligand C$_6$Cl$_2$F$_3$ is higher than that of Cl.[22] Moreover, the Pd–P lengths for **4** are very different from those found in chloro complexes, but fairly close to those found for *cis*-[PdMe$_2$(PMePh$_2$)$_2$] (2.321(1), 2.326(1) Å),[15] suggesting comparable *trans* influences for Pf and Me.

Behavior of complex 1 in THF solution

The existence of equilibria between aquo-complexes and complexes containing weak ligands is fairly common in group 10 cationic complexes,[23,24] but has been scarcely studied in neutral complexes.[12,13,25] When complex **1** is dissolved in THF, the residual water contained in the solvent competes with the coordinated THF for the palladium center. This substitution reaction is not observable by NMR spectroscopy at room temperature because the fast exchange between coordinated water and THF gives averaged signals, but at 223 K the signals of **1** and *cis*-[PdRf$_2$(THF)(OH$_2$)] (**11**) are clearly separated (Fig. 2).[12,13,26] The content in water of the THF solvent handled in the calorimetry experiments, determined by Karl-Fischer titration, is 2.70×10^{-3} M. The experiment shown in Fig. 2 was carried out with a sample that, in the absence of substitution rearrangement, should be 7.4×10^{-3} M in **1**. The equilibrium concentrations at 223 K, (calculated from the integrated signals) were 6.4×10^{-3} M for **1** and 1.0×10^{-3} M for **11**, which gives an estimation of $K_{eq} = 1.1 \times 10^3$, and $\Delta G_{eq} = -13$ kJ mol^{-1}.[27,28] From now on, we will use *cis*-[PdRf$_2$(solv)$_2$] to refer to this mixture of *cis*-[PdRf$_2$(THF)$_2$] and *cis*-[PdRf$_2$(THF)(OH$_2$)], formed when pure *cis*-[PdRf$_2$(THF)$_2$] is dissolved in THF under working conditions.

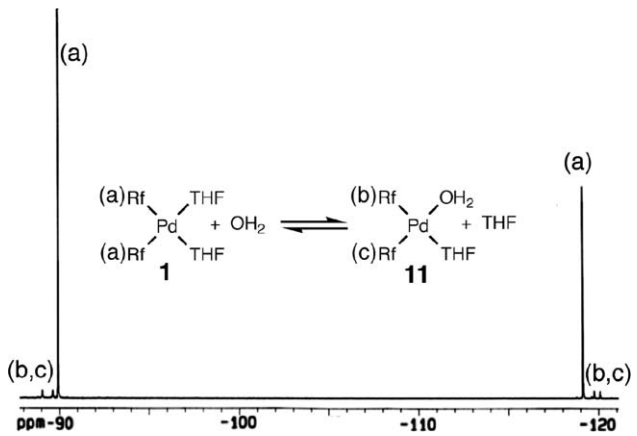


Fig. 2 ^{19}F NMR spectrum of **1** in THF at −50 °C, showing minor signals of **11**.

Calorimetric measures of substitution reactions

Ligand substitution reactions (eqn (1)) were carried out in THF at 271.3 K, under atmospheric pressure of dry nitrogen, using a 7.42×10^{-3} M concentration of *cis*-[PdRf$_2$(solv)$_2$], and a L : Pd = 10 : 1 ratio of added ligand L to ensure a fast and essentially complete shift of the equilibrium to *cis*-[PdRf$_2$L$_2$]. In order to compensate for the dilution heat, an identical solution of ligand was added to pure THF in the reference cell. After each experiment was calorimetrically complete, ^{19}F and ^{31}P NMR of the mixture were registered at the working temperature, without dilution of the sample, to verify that the reaction had finished.

Table 2 Enthalpies of substitution (kJ mol^{-1}) in the reactions of eqn (1), corrected data for *cis*-[PdRf$_2$(THF)$_2$], and NMR data of the products

Entry	L	$-\Delta H$/kJ mol^{-1} (standard deviation)[a]	$-\Delta H$/kJ mol^{-1} corrected[b]	^{19}F NMR (ppm)[c]	^{31}P NMR (ppm)[c]
1	PPh_3	109 (4)	110	−89.1, −120.9	19.4
2	$PCyPh_2$	126 (6)	127	−87.6, −120.3	19.8
3	$PMePh_2$	160 (8)	160	−88.8, −121.3	4.3
4	PMe_3	187 (2)	187	−88.7, −120.3	−18.0
5	$\frac{1}{2}$dppe	154 (2)	154	−88.2, −120.9	49.2
6	$\frac{1}{2}$dppf	143 (1)	143	−89.1, −120.8	17.0
7	$AsPh_3$	72 (2)	72	−88.5, −120.4	—
8	$AsMePh_2$	96 (2)	96	−88.2, −120.6	—
9	$SbPh_3$	60 (3)	60	−86.8, −119.8	—

[a] Substitution on *cis*-[PdRf$_2$(solv)$_2$]. Each data point is the average of three experiments. [b] Substitution starting on *cis*-[PdRf$_2$(THF)$_2$] (calculated data). [c] The NMR of the reaction solution was registered at 273.3 K, using a coaxial tube containing deuterated acetone for deuterium-lock.

$$cis\text{-}[PdRf(solv)_2] + 2L \rightleftharpoons cis\text{-}[PdRf_2L_2] + 2solv \quad (1)$$

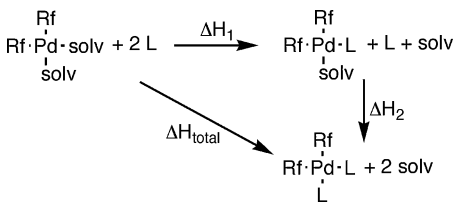
In order to correct the measured heat for the presence of complex **11** in the initial solution, we tried to measure the enthalpy of substitution of THF by water, applying eqn (1) for OH_2 as ligand. However, the heat released in the reaction of *cis*-[PdRf$_2$(solv)$_2$] with OH_2 was too small for accurate integration of the curve obtained in the calorimeter. Alternatively, the heat of the substitution reaction of *cis*-[PdRf$_2$(OH$_2$)$_2$] prepared *in situ* (see Experimental) with PPh_3 was measured (93(3) kJ mol^{-1}). This value, together with the enthalpy of substitution on *cis*-[PdRf$_2$(solv)$_2$] with PPh_3 (109(4) kJ mol^{-1}), allows calculation of the reaction heat of the substitution of the two coordinated THF ligands by two OH_2 molecules ($\Delta H = -17$ kJ mol^{-1}). Since the concentrations of *cis*-[PdRf$_2$(THF)$_2$] and *cis*-[PdRf$_2$(THF)(OH$_2$)] in the initial mixture are known from NMR, it was possible to calculate values of the reaction heats corrected for the percentage of substitution of one THF for one OH_2 for all the ligands employed in this work (Table 2).[29] It turned out that the differences between the experimental data measured on *cis*-[PdRf$_2$(solv)$_2$] and the corrected data for *cis*-[PdRf$_2$(THF)$_2$] are equal within experimental error, so that in fact the corrections can be neglected.

Comparing the results collected in Table 2, a large decrease in reaction heat is observed for analogous ligands differing only in the donor atom (Table 2, entries 1, 7, 9 and entries 3, 8). Relative to PPh_3, $AsPh_3$ releases 66% of heat, and $SbPh_3$ only 55%. This effect, qualitatively well known but not previously quantified, is explained by the loss of bond directionality in group 15 ligands when going down in the group, due to the increasing s orbital participation of the donor pair.[30] This loss of σ bond energy is not compensated by a gain in π backbonding, due to the high stability of the filled d orbitals in Pd(II).[31] The closest system previously studied, the substitution of THF in the cation *trans*-[PtMe(THF)(PMePh$_2$)$_2$]$^+$, shows a similar but more steep descent in bond energy, probably because the cationic Pt(II) is harder than the neutral Pd(II): the energy involved in the substitution by $SbPh_3$ in the Pt complex is only a 31% of that for PPh_3.[8a] The reaction heats for simple phosphines $PPh_3 < PMePh_2 < PMe_3$ (Table 2, entries 1, 3, 4) or arsines $AsPh_3 < AsMePh_2$ (entries 7, 8) follow the trend imposed mostly by the ligand basicity, according to the different substituents, whereas the sequence $PCyPh_2 < PMePh_2$ (entries 2 and 3) reflects mostly the unfavorable effect of steric encumbrance associated to the bulk Cy compared to the small Me (see, however, Discussion below).

The ligand–metal orbital overlap also depends on the coordination angles, which in *cis* complexes are often different from the ideal 90°. This can be particularly important when bulky ligands force wider angles (probably the case of entry 2), and when chelating ligands impose a constrained bite angle, whether larger or smaller. Thus, comparing the electronically similar dppe and $PMePh_2$ ligands, both P–Pd–P coordination angles are about 5° from 90° (Table 1). Consistently, their enthalpies for the substitution of two THF ligands (Table 2, entries 3 and 5) are quite similar (just 6 kJ mol^{-1} lower for dppe). The higher geometrical constraint for dppf[32] leads to a bite angle of 99° in **7** (Table 1), and a further enthalpy decrease of 10.5 kJ mol^{-1} compared to dppe.[33] Interestingly, ΔH for dppf is still almost 33 kJ mol^{-1} larger than for PPh_3, suggesting that the ferrocenyl substituent on phosphorus is more similar to an alkyl than to an aryl.

Analysis of consecutive reactions

The heats collected in Table 1, measured for different L ligands according to reaction (1), are in fact the result of two consecutive substitution reactions (Scheme 2)



Scheme 2

A stepwise direct experimental determination of each of the two consecutive enthalpies involved was not possible because the addition of only one equivalent of L per palladium leads to a mixture in equilibrium of *cis*-[PdRf$_2$L(solv)], *cis*-[PdRf$_2$L$_2$], and starting material *cis*-[PdRf$_2$(solv)$_2$]. The addition of more than one equivalent of L leads to increasing proportions of *cis*-[PdRf$_2$L$_2$]. Fortunately the mono- and disubstituted products give separated signals in ^{19}F NMR, allowing for independent integration.

With these data in hand, the heat measured in any substitution reaction can be correlated with the enthalpies of the two consecutive reactions and the concentrations of products in equilibrium.[34] The enthalpies of the consecutive substitutions ΔH_1 and ΔH_2 can be obtained from the slope and the *y*-intercept of the linear plot Q_i/n_{1I} *versus* n_{2I}/n_{1I}. For the experiment *i*, Q_i is the observed heat

released, n_{1f} is the number of moles of *cis*-[$PdRf_2L$(solv)] formed during the reaction, and n_{2f} is the number of moles of *cis*-[$PdRf_2L_2$] in the final equilibrium (see Experimental for more details). This procedure was applied to experiments performed with PPh_3 and $PCyPh_2$. The values calculated for the two consecutive reactions, ΔH_1 and ΔH_2, obtained from the linear plots in Fig. 3, are consistent with the data directly measured ΔH_{total}. In effect, the sum $\Delta H_1 + \Delta H_2$ (−109 kJ mol^{-1} for PPh_3 and −125 kJ mol^{-1} for $PCyPh_2$) is almost identical to the experimental value ΔH_{total} (−109(4) and −126(8) kJ mol^{-1}, respectively; Table 2).

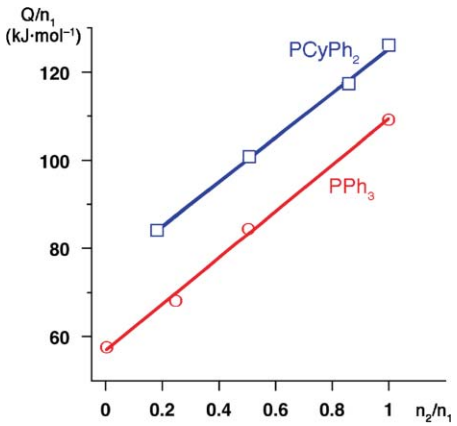


Fig. 3 Linear plot Q_i/n_1 *versus* n_2/n_1 from values obtained by partial substitution experiments with PPh_3 and $PCyPh_2$.

Influence of steric hindrance on the bond energy

Two parameters proposed by Tolman are used to classify ligand properties:[35] ligand hindrance is estimated by the Tolman "cone angle", and electron richness by the Tolman electronic parameter (TEP). The sequence of enthalpy values observed for the substitution reactions with monodentate phosphines (Table 2) is PMe_3 > $PMePh_2$ > $PCyPh_2$ > PPh_3, and must be the overall reflection of electronic and steric influences. The cone angles and TEP values for these phosphines are: PMe_3 = 118°, 2064.1 cm^{-1}; $PMePh_2$ = 136°, 2067.0 cm^{-1}; $PCyPh_2$ = 153°, 2064.8 cm^{-1}; PPh_3 = 145°, 2068.9 cm^{-1}.

It is very likely that the influence of the steric hindrance contribution will be relatively larger in the square-planar complexes studied here (L–Pd–L, angle about 90°, two non-small non-linear ligands) than in the less crowded tetrahedral $Ni(CO)_3L$ (L–Ni–CO, angle of about 109°, and one small linear ligand, CO), which are the kind of complexes used as reference to define TEP.[36] The values of the first and second substitution enthalpies found for $PCyPh_2$ and PPh_3 give a nice illustration of the complex influence of steric and electronic properties on bond energy. In the absence of steric factors, the bond energy should depend on the electronic properties of the ligand. The order of ΔH_{total} values found for the double substitution reaction is $PCyPh_2$ > PPh_3 (Table 2) would be consistent with the expectations from the electronic properties. An inspection of the consecutive substitution enthalpies affords a richer view of the process. Fig. 4 (lower plot) shows graphically the enthalpy data for the two ligands. The ratio $\Delta H_2/\Delta H_1$ is about 0.91 for PPh_3, but only about 0.66 for $PCyPh_2$. In fact ΔH_1 is considerably larger for $PCyPh_2$, but ΔH_2 is larger for

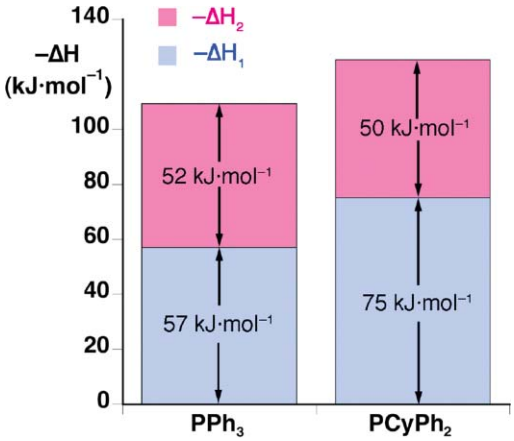


Fig. 4 Plot of first and second substitution enthalpies (ΔH_1 and ΔH_2) for PPh_3 and $PCyPh_2$.

PPh_3. In simple terms one could say that, although $PCyPh_2$ is a stronger ligand and the formation of *cis*-[$PdRf_2L_2$] is, overall, more exothermic for L = $PCyPh_2$, the replacement of one L in *cis*-[$PdRf_2L_2$] to give *cis*-[$PdRf_2L$(solv)], releasing one L, is thermally less costly for L = $PCyPh_2$, in spite of the commonly accepted idea that it is a "better donor ligand" than PPh_3. The structural data of similar complexes (particularly the P–Pd–P angles) suggest that there should be very little crowding in complex **2**,[14] so the small decrease in ΔH from the first to the second substitution (ΔH_2 is 9% smaller than ΔH_1) is probably caused mostly by the lowering in Pd electrophilicity after one PPh_3 has been coordinated.

For $PCyPh_2$, however, the effect observed (33%) is much larger than one would probably expect on electronic grounds, indicating that much of this reduction must be due to the steric crowding effect. It is interesting to note that the increase in cone angle is not that big (PPh_3 = 145°; $PCyPh_2$ = 153°), but produces a large effect in *cis*-[PdR_2L_2] complexes. In fact, further increase of steric hindrance of the ligand greatly disfavor its coordination ability, and *cis*-[$PdRf_2(PCy_3)_2$] could not be prepared.

Kinetic study of ligand substitution

According to the results discussed above, and assuming that the ligand exchange equilibrium between *cis*-[$PdRf_2(PCyPh_2)_2$] and *cis*-[$PdRf_2(PPh_3)_2$] is dominated by enthalpy, a preference for the formation of the mixed complex *cis*-[$PdRf_2(PPh_3)(PCyPh_2)$] might be expected. For the same reason, since the reaction *cis*-[$PdRf_2$(solv)$_2$] + 2 L does not lead to complete solvent substitution, one could expect that on dissolving any of the two phosphine complexes above in THF, the equilibrium containing some *cis*-[$PdRf_2$(solv)$_2$] and some *cis*-[$PdRf_2L$(solv)] should be established. However, none of these rearrangements was observed with the complexes *cis*-[$PdRf_2(PCyPh_2)_2$] or *cis*-[$PdRf_2(PPh_3)_2$]. In effect, 1 : 1 mixtures of *cis*-[$PdRf_2(PCyPh_2)_2$] and *cis*-[$PdRf_2(PPh_3)_2$] did not rearrange perceptibly even after long periods of time, and any of these complexes remained unaffected after a long time in THF. This inertness towards ligand substitution precluded assessing experimentally the relative thermodynamic ease of substitution predicted for each of the two phosphines. The very different rates of the ligand exchange for the fast forward reaction on *cis*-[$PdRf_2L$(solv)], and slow reverse reaction on *cis*-[$PdRf_2(PRPh_2)_2$]

(R = Ph, Cy) suggests that, whether the mechanism is associative or dissociative, the elongation of the bond to the leaving ligand must be important in the transition state. This is why the reaction is fast when the leaving group is a weak THF ligand, but slow when the leaving ligand is a phosphine.

The ligand substitution reactions were examined then for the ligand exchange *cis*-[$PdRf_2L_2$] + 2 L′, L and L′ being the two phosphines. In both cases the formation of *cis*-[$PdRf_2LL'$] and a minute amount of *cis*-[$PdRf_2L'_2$] was observed. The reaction (in THF at room temperature) was very slow, and after three days the reaction was still far from equilibrium, while some decomposition started to interfere with the experiment. This behavior precluded the direct determination of the equilibrium constants, but at least the kinetics of these slow substitutions could be measured at 323 K. It turned out that the substitution of PPh_3 by $PCyPh_2$ in *cis*-[$PdRf_2(PPh_3)_2$] to give *cis*-[$PdRf_2(PPh_3)(PCyPh_2)$], and that of $PCyPh_2$ by PPh_3 in *cis*-[$PdRf_2(PCyPh_2)_2$], take place with almost the same rate (0.022 and 0.037 min^{-1} respectively), and with similar activation free energies (100.6 and 99.1 kJ mol^{-1}). The difference between these $\Delta G^{\ddagger}$ (1.5 kJ mol^{-1}) values is essentially identical to the difference in substitution enthalpy of the first ligand substitution by THF determined calorimetrically (2 kJ mol^{-1}) supporting the idea that both substitutions have the same entropic influence. This does not help to suggest any substitution mechanism over another. However, it is not unreasonable that a dissociative mechanism could be preferred, as the extreme crowding in the pentacoordinated intermediate of an associative substitution mechanism would make it even higher in energy. Dissociative mechanisms in related Pt complexes were proposed and supported by Romeo,[37] and have been suggested for substitution reactions in hindered *cis*-[$Pd(Fmes)_2(SR_2)_2$] (Fmes = 2,4,6-tris(trifluoromethyl)phenyl) complexes.[38]

Conclusions

The enthalpies of substitution in *cis*-diarylpalladium complexes follow the expected trends considering the electronic and steric parameters used to describe the behavior of ligands. However, for the bulkiest ligands there are large differences between the energy involved in the first and the second substitution, due to the steric hindrance imposed by the first ligand over the second. Therefore, the second substitution enthalpy may differ very significantly from the values one could guess from parameters determined on simpler systems, such as Tolman's parameters. The results also show that there is no straightforward relationship between the substitution enthalpy and the kinetics of the substitution reaction: although enthalpy would favor the release of bulky ligands, hindrance can induce inertness towards associative substitutions, leading to dissociative or interchange dissociative mechanisms that, when involving strong ligands, may require high reaction temperatures for the kinetics to be appreciable.

Experimental

General comments

All reagents were purchased from commercial sources and used as received. Solvents were dried by known procedures and distilled under nitrogen prior to use. THF was refluxed over sodium and distilled under nitrogen; benzophenone was used as a moisture indicator. ^{1}H NMR (300.16 MHz) and ^{19}F NMR (282.4 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with a VT-100 variable temperature probe. Chemical shifts are reported in ppm from tetramethylsilane (^{1}H), or CCl_3F (^{19}F), with positive shifts downfield, at ambient probe temperature unless otherwise stated. In the ^{19}F NMR spectra registered in non-deuterated solvents, a coaxial tube containing acetone-d_6 was used to maintain the lock ^{2}H signal, and the chemical shifts are reported from the CCl_3F signal in deuterated acetone. Combustion CHN analyses were made on a Perkin-Elmer 2400 CHN microanalyzer. Infrared spectra were recorded on a Perkin-Elmer 843 apparatus (range 4000–200 cm^{-1}) with Nujol mulls between polyethylene sheets or in dichloromethane solution between NaCl plates. Ligand $AsMePh_2$[39] and complexes *cis*-[$Pd(C_6Cl_2F_3)_2(THF)_2$] (**1**), *cis*-[$Pd(C_6Cl_2F_3)_2(COD)_2$] (COD = 1,5-cyclooctadiene), *cis*-[$Pd(C_6Cl_2F_3)_2(PPh_3)_2$] (**2**), and *cis*-[$Pd(C_6Cl_2F_3)_2(PMe_3)_2$] (**5**) were prepared by published methods.[12] Complex (**1**), used repeatedly for the calorimetric studies, was prepared on a large scale in order to use the same material for all the experiments.

Characterization of the mixture *cis*-[$PdRf_2(solv)_2$]

A solution of complex *cis*-[$PdRf_2(THF)_2$] (4.8 mg, 7.4 μmol) in THF (1.0 mL) was prepared. Two singlets are observed in ^{19}F NMR at 271.3 K, which are due respectively to F_{ortho} and F_{para} of *cis*-[$PdRf_2(THF)_2$] and *cis*-[$PdRf_2(THF)(OH_2)$] in fast exchange equilibrium. ^{19}F NMR (THF, 271.3 K): $\delta = -89.8$ (s, 4F, F_{ortho}), −119.1 (s, 2F, F_{para}). At 223 K both complexes are observed, with concentrations of 6.4×10^{-3} M and 1.0×10^{-3} M for *cis*-[$PdRf_2(THF)_2$] and *cis*-[$PdRf_2(THF)(OH_2)$], respectively. ^{19}F NMR (THF, 223 K): $\delta = -89.1$ (s, 2F, F_{ortho} of *cis*-[$PdRf_2(THF)(OH_2)$]), −89.6 (s, 2F, F_{ortho} of *cis*-[$PdRf_2(THF)(OH_2)$]), −89.9 (s, 4F, F_{ortho} of *cis*-[$PdRf_2(THF)_2$]), −119.2 (s, 2F, F_{para} of *cis*-[$PdRf_2(THF)_2$]), −119.8 (s, 1F, F_{para} of *cis*-[$PdRf_2(THF)(OH_2)$]), −120.1 (s, 1F, F_{para} of *cis*-[$PdRf_2(THF)(OH_2)$]).

Calorimetric measurements

Calorimetric measurements were performed using an Omnical reaction calorimeter. The instrument contains a calorimeter that compares the heat released or consumed in a sample vessel to an empty reference vessel, and an internal magnetic stirrer. The vessels were 16 mL 21 mm × 70 mm borosilicate screw-thread vials fit with open top screw caps and PTFE septa, and charged with Teflon stir bars. The temperature of the calorimeter was held constant using a Julabo F25 circulator, ensuring that the reaction would proceed under isothermal conditions. The temperature of the circulating system was set at 268 K. After 12 h, the temperature in the calorimeter was constant and stabilized in the final value 271.3 K. In a typical experiment, the reaction vessel was charged with 19.30 mg of *cis*-[$PdRf_2(THF)_2$] (29.67 μmol) and 2 mL of THF, and the reference vessel with 2 mL of THF. In the sample injection ports of both vessels were placed syringes containing 2 mL of solution of the ligand (296.7 mmol for monodentate ligands, 148.35 mmol for bidentate ligands) in THF. The system was allowed to reach thermal equilibrium for at least one hour. Then, the solution of ligand was simultaneously injected in both vessels. When the reaction finished, an aliquot of the solution was

placed in a NMR tube containing a coaxial capillary tube with deuterated acetone, and ^{19}F (and ^{31}P NMR) spectra were recorded to verify the absence of side reactions.

To measure the heat released in the substitution reaction of PPh_3 with *cis*-[$PdRf_2(OH_2)_2$] the experiment was similar, but used a 2.0 M solution of water in THF instead of pure THF as solvent. Prior to this experiment, a solution of *cis*-[$PdRf_2(THF)_2$] (29.67 μmol) in a 2.0 M solution of water in THF was checked by NMR to make sure that *cis*-[$PdRf_2(OH_2)_2$] was the only complex in solution: ^{19}F NMR (THF, 271.3 K): $\delta = -88.7$ (s, 4F, F_{ortho}), −121.0 (s, 2F, F_{para}).

Evaluation of consecutive reaction enthalpies

The calorimetric experiments were performed as described above. In a double substitution process of the type shown in Scheme 2, the reaction of the starting complex *cis*-$PdRf_2(solv)_2$ with more than one equivalent of ligand L lead to the formation of n_1 mol of (*cis*-[$PdRf_2L(solv)$] + *cis*-[$PdRf_2L_2$]) and n_2 mol of [$PdRf_2L_2$]. Note that n_1 is the sum of the mol of the complexes *cis*-[$PdRf_2L(solv)$] and *cis*-[$PdRf_2L_2$] because both have suffered the first substitution, while n_2 is just the amount of *cis*-[$PdRf_2L_2$].

$$cis\text{-}[PdRf_2(solv)_2] + L \rightarrow cis\text{-}[PdRf_2L(solv)],\ \Delta H_1$$

$$cis\text{-}[PdRf_2L(solv)] + L \rightarrow cis\text{-}[PdRf_2L_2],\ \Delta H_2$$

$$cis\text{-}[PdRf_2(solv)_2] + 2L \rightarrow cis\text{-}[PdRf_2L_2],\ \Delta H = \Delta H_1 + \Delta H_2$$

The concentrations of *cis*-[$PdRf_2L(solv)$] and *cis*-[$PdRf_2L_2$] were obtained from their integrated signals in the ^{19}F NMR spectra, registered at 271.3 K from a aliquot of the solution employed in the calorimetric experiment. The overall heat released by the reaction Q, measured as the integral of the calorimeter signal, is the sum of the heat released in steps 1 and 2 (q_1 and q_2).

$$Q = q_1 + q_2 = -n_1\Delta H_1 - n_2\Delta H_2$$

$$\frac{Q}{n_1} = -\Delta H_1 - \frac{n_2}{n_1}\Delta H_2$$

A plot of Q/n_1 *versus* n_2/n_1 gives a straight line with slope $-\Delta H_2$ and y-intercept $-\Delta H_1$.

Synthesis and NMR data of the palladium complexes

***cis*-[$PdRf_2(PCyPh_2)_2$] (3).** To a stirred solution of [$PdRf_2$(COD)] (111 mg, 0.181 mmol) in THF (20 mL), was added $PCyPh_2$ (110 mg, 0.409 mmol). After 30 min the solution was concentrated to 5 mL and 10 mL of n-hexane were added. Further evaporation of the solvent yielded the product as white crystals. Yield 179 mg (80%). Anal. calcd for $C_{48}H_{42}Cl_4F_6P_2Pd$ (%): C 55.28, H 4.06. Found: C 54.87, H 3.91. ^1H NMR ($CDCl_3$, 293 K): $\delta = 7.38$ (m, 4H, Ph), 7.19 (m, 8H, Ph), 7.00 (m, 8H, Ph), 1.58 (m, 10H, Cy), 0.91 (m, 8H, Cy), 0.54 (m, 4H, Cy). ^{19}F NMR ($CDCl_3$/THF, 293 K): $\delta = -88.5/-87.3$ (s, 4F_{ortho}), −120.0/−120.2 (s, 2F_{para}). ^{31}P NMR ($CDCl_3$/THF, 293 K): $\delta = 19.6/19.8$.

***cis*-[$PdRf_2(PMePh_2)_2$] (4).** To a stirred solution of [$PdRf_2$(COD)] (428 mg, 0.697 mmol) in THF (30 mL), was added $PMePh_2$ (5.2 mL of a 0.3 M solution in THF, 1.6 mmol). After 30 min the solution was concentrated to 10 mL and n-hexane (10 mL) was added. Further evaporation of the solvent yielded the product as white crystals. Yield 569 mg (90%). Anal. calcd for $C_{38}H_{26}Cl_4F_6P_2Pd$ (%): C 50.33, H 2.94. Found: C 50.15, H 2.94. ^1H NMR ($CDCl_3$, 293 K): $\delta = 7.4$–7.2 (m, 20H, Ph), 1.51 (m, 3H, Me). ^{19}F NMR ($CDCl_3$/THF, 293 K): $\delta = -88.9/-88.7$ (t, $J = 7.6/7.6$ Hz, 4F_{ortho}), −120.7/−121.2 (s, 2F_{para}). ^{31}P NMR ($CDCl_3$/THF, 293 K): $\delta = 3.6/4.3$ (m).

[$PdRf_2$(dppe)] (6). Prepared as described for **4** but using dppe (302 mg, 0.758 mmol) instead of $PMePh_2$. Yield 595 mg (94%). Anal. calcd for $C_{38}H_{24}Cl_4F_6P_2Pd$ (%): C 50.45, H 2.67. Found: C 50.49, H 3.03. ^1H NMR ($CDCl_3$, 293 K): $\delta = 7.6$–7.3 (m, 20H, Ph), 2.36 (s, 2H, CH_2–CH_2), 2.29 (s, 2H, CH_2–CH_2). ^{19}F NMR ($CDCl_3$/THF, 293 K): $\delta = -89.4/-88.0$ (t, $J = 7.6/7.6$ Hz, 2F_{ortho}), −120.3/−120.8 (s, 1F_{para}). ^{31}P NMR ($CDCl_3$/THF, 293 K): $\delta = 48.0/49.1$ (m).

[$PdRf_2$(dpp(f)] (7). To a stirred solution of [$PdRf_2$(COD)] (180 mg, 0.294 mmol) in THF (10 mL), was added dppf (180.3 mg, 0.758 mmol). After 30 min the solution was concentrated to 5 mL and n-hexane (10 mL) was added. Further evaporation of the solvent yielded the product as yellow crystals. Yield 275 mg (88%). Anal. calcd for $C_{46}H_{28}Cl_4F_6FeP_2Pd$ (%): C 52.09, H 2.66. Found: C 52.10, H 2.94. ^1H NMR ($CDCl_3$, 293 K): $\delta = 7.57$ (m, 8H, Ph), 7.46 (m, 4H, Ph), 7.34 (m, 8H, Ph), 4.34 (m, 8H, Cp). ^{19}F NMR ($CDCl_3$/THF, 293 K): $\delta = -90.1/-88.9$ (t, $J = 7.6/7.6$ Hz, 4F_{ortho}), −120.5/−120.7 (s, 2F_{para}). ^{31}P NMR ($CDCl_3$/THF, 293 K): $\delta = 16.4/16.9$ (m).

***cis*-[$PdRf_2(AsPh_3)_2$] (8).** To a stirred solution of [$PdRf_2$(COD)] (210 mg, 0.342 mmol) in THF (20 mL), was added $AsPh_3$ (231.8 mg, 0.757 mmol). After 30 min the solution was concentrated to 5 mL and n-hexane (10 mL) was added. Further evaporation of the solvent yielded the product as white crystals. Yield 326.4 mg (85%). Anal. calcd for $C_{48}H_{30}As_2Cl_4F_6Pd$ (%): C 51.53, H 2.70. Found: C 51.18, H 2.67. ^1H NMR ($CDCl_3$, 293 K): $\delta = 7.4$-7.2 (m, 20H, Ph). ^{19}F NMR ($CDCl_3$/THF, 293 K): $\delta = -89.4/-88.3$ (s, 4F_{ortho}), −120.2/−120.3 (s, 2F_{para}).

***cis*-[$PdRf_2(AsMePh_2)_2$] (9).** To a stirred solution of [$PdRf_2$(COD)] (139 mg, 0.226 mmol) in THF (20 mL) was added $AsMePh_2$ (122.0 mg, 0.500 mmol). After 30 min, the solution was concentrated to 5 mL and Et_2O (10 mL) was added. Further evaporation of the solvent yielded the product as white crystals. Yield: 162 mg (86%). Anal. calcd for $C_{38}H_{26}As_2Cl_4F_6Pd$ (%): C 45.89, H 2.63. Found: C 45.72, H 2.73. ^1H NMR ($CDCl_3$, 293 K): $\delta = 7.4$–7.2 (m, 20H, Ph), 1.38 (s, 6H, Me). ^{19}F NMR ($CDCl_3$/THF, 293 K): $\delta = -89.3/-88.1$ (s, 4F_{ortho}), −119.9/−120.4 (s, 2F_{para}).

***cis*-[$PdRf_2(SbPh_3)_2$] (10).** A stirred solution of [$PdRf_2$(COD)] (257 mg, 0.418 mmol) in THF (20 mL), was cooled to 0 °C. Then $SbPh_3$ (326.3 mg, 0.924 mmol) was added. After 45 min the solution was concentrated to 10 mL and n-hexane (15 mL) was added. Further evaporation of the solvent yielded the product as white crystals. Yield 456 mg (90%). Anal. calcd for $C_{48}H_{30}Cl_4F_6PdSb_2$ (%): C 47.55, H 2.49. Found: C 47.23, H 2.76. ^1H NMR ($CDCl_3$, 293 K): $\delta = 7.33$ (m, 12H, Ph), 7.21 (m, 18H, Ph). ^{19}F NMR ($CDCl_3$/THF, 293 K): $\delta = -87.8/-86.7$ (s, 4F_{ortho}), −119.5/−119.7 (s, 2F_{para}).

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28 In order to use these data, measured at 223 K, in studies on substitution reactions on *cis*-[PdRf$_2$(solv)$_2$] (solv = THF or OH$_2$) carried out at 271.3 K, we assume that the variation in ΔS can be neglected; then $\Delta G_{223\,K} \approx \Delta G_{271.3\,K}$. The equilibrium constant and concentrations of **1**

and **2** at 271.3 K calculated from $\Delta G_{271.3\,K}$ are: $K_{eq}(271.3) = 3.2 \times 10^2$, $[\mathbf{1}] = 7.0 \times 10^{-3}$ M, $[\mathbf{2}] = 0.4 \times 10^{-3}$ M.
29 The correction has been done using the concentrations of $[PdRf_2(solv)_2] = [PdRf_2(THF)_2] + [PdRf_2(THF)(OH_2)]$ found in the spectrum at 223 K. We need to assume that the first substitution of a THF on *cis*-$[PdRf_2(THF)_2]$ (which yields *cis*-$[PdRf_2(THF)(OH_2)]$), has an enthalpy not significantly different to the second substitution (which yields *cis*-$[PdRf_2(OH_2)_2]$). Since the ^{19}F NMR spectrum (Fig. 2) shows that only one THF has been substituted by one OH_2, a correction of 8.5 kJ mol^{-1} was made.
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