Observation of a Slow Dissociative Process in Palladium(II) Complexes

Juan A. Casares, Silverio Coco, Pablo Espinet,* and Yong-Shou Lin

Departamento de Quimica Inorganica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain

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The dynamic behavior of complexes $[Pd(C_6F_5)X(SPPy_nPh_{3-n})]$ (Py = pyridin-2-yl; X = Br, n = 1 (1), 3 (3); n = 2, X = Cl (2a), Br (2b), I (2c)) has been studied by NMR spectroscopy. Complex 1 has a S,N-chelating ligand and shows no isomers. Complexes 2 show two isomers, N,N- and N,S-bonded, the latter being dominant (>95%). Rotation of the C_6F_5 group in the N,S-isomers in CDCl₃ occurs slowly with ΔH^{\ddagger} (kJ mol⁻¹) = 60.0 (2a), 57.1 (2b), 50.2 (2c) and ΔS^{\ddagger} (J K⁻¹ mol⁻¹) = -35.8 (2a), -37.5 (2b), -51.1 (2c). Evidence strongly supports that this rotation is severely hindered in a square-planar complex and occurs in a contact ion pair $[Pd(C_6F_5)(SPPy_2Ph-N,S)] \cdot X$ formed by halide dissociation. Complex 3 shows also two isomers, and its N,N-isomer shows apparent C_6F_5 rotation corresponding in reality to exchange of the Py group trans to the Pd-C bond and the uncoordinated Py group. The structure of $[Pd(C_6F_5)Br(SPPy_2Ph-N,S)]$ has been studied by X-ray diffraction: $P2_1/c$, a = 8.273(2) Å, b = 14.240(2) Å, c = 19.547(4) Å, $\beta = 95.10(2)^\circ$, V = 2293.6(7) Å³, Z = 4.

Introduction

A dissociative process, usually of a neutral ligand, is often invoked as the initial step in many reactions involving Pd(II), Pt(II), and other square-planar d⁸ organometallic complexes. This preliminary dissociation enables β -H elimination,^{1a-c} isomerization,^{1d-j} reductive elimination,^{1d-i} or exchange reactions^{1k} to occur. Surprisingly only limited thermodynamic data are available after much excellent work, and support for the dissociation step comes mostly from observation of rateretarding effects by added ligands.

For Pt(II) clear-cut evidence for dissociative mechanisms in simple ligand-substitution processes, which are always associative in classical complexes, has been provided by the study of the reactions *cis*-[PtR₂L₂] + 2*L = cis-[PtR₂*L₂] + 2L (R = Ph or Me, L = Me₂SO; R = Ph, L = SMe₂; *L = labeled L) for which clearly positive ΔV^{\ddagger} values were found.² These results show that the presence of Pt-C bond can produce a sharp changeover of reaction pathways from associative modes of activation in classical complexes to dissociative in organometallics. More recently, the displacement of thioether by pyridines has been demonstrated to be dissociative for [PtPh₂(SEt₂)₂] but associative for [PtPh₂-(SEt₂)(CO)].^{2c} The presence in the latter of a LUMO

perpendicular to the plane, prone to the nucleophilic attack, is the reason for the changeover of mechanism. Finally, the considerable acceleration in rate observed for the substitution of the aqua ligand trans to the Pt-C bond in the orthoplatinated complex $[Pt{C_6H_3X(CH_2 NMe_2$ ($NC_5H_4SO_3-3$)(H_2O)], largely due to a strong decrease in ΔH^{\ddagger} , is not associated with a changeover in mechanism, which is still associative.³ Altogether the occurrence of dissociative substitutions in Pt(II) organometallic complexes seems to be "a combined result of ground-state destabilization and of a concurrent increase of electron density at the metal, preventing the approach of nucleophiles".^{2a} On the other hand, studies by Romeo et al. on the uncatalyzed cis to trans isomerization of complexes of the type [PtRXL₂] in alcohol solvents and on some other processes have accumulated much consistent evidence for the operation of dissociative mechanisms usually involving halide dissociation^{4a} but sometimes L dissociation.^{4b}

The thermodynamic data in the literature for dissociative processes in Pd(II) are very scarce and recent and mostly refer to the dissociation of a neutral ligand: Sen *et al.* have determined the values of ΔG° , ΔH° , and ΔS° for the reaction Pd(COCOPh)Cl(PPh₃)₂ = Pd-(COCOPh)Cl(PPh₃) + PPh₃.⁵ ΔG^{\dagger} values have been reported on the mechanism of apparent rotation in (π allyl)-palladium complexes with bidentate nitrogen ligands, which seems to occur *via* cleavage of a Pd-N bond although some aspects remain obscure.⁶ ΔH^{\ddagger} and ΔS^{\ddagger} values have been reported in another recent paper concerning the *cis*-*trans* isomerization of [Pd(C₆F₅)₂-(tht)₂] (tht = tetrahydrothiophene) which involves tht

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Figure 1. General schematic representation of the N,S-chelated species, showing the fast envelope shift making the five-membered ring appear as coplanar with the coordination plane on the NMR time scale.

dissociation.⁷ Finally, as a result of the study of the thermolysis behavior of *trans*-[PdEt(OAc)(PMe₃)₂] the following values were obtained for the dissociation of OAc⁻ in EtOH: $\Delta H^{\ddagger} = 41.4 \text{ kJ mol}^{-1} \text{ and } \Delta S^{\ddagger} = -171.4 \text{ J} \text{ K}^{-1} \text{ mol}^{-1.8}$ The large negative ΔS^{\ddagger} value was interpreted as the dissociation of the acetate being assisted by solvent coordination.

Whenever a dissociation process is followed by subsequent steps leading to products different from the starting materials (e.g., isomers, coupling products of a thermal decomposition, products of a ligand exchange, etc.), there is some uncertainty whether the thermodynamic parameters determined are related to the dissociative step (assumed to be the rate-determining step) or to a subsequent step in the whole process (if that assumption is not correct). The observation of a rate retardation by added ligand does not prove that the dissociation is the rate-determining step, since a masslaw effect will retard the reaction no matter what the rate-determining step is in the absence of added ligand (moreover, there is also the ambiguity of whether the rate retardation comes from blocking the formation of a three-coordinate species or from the formation of an unreactive five-coordinate species). In order to avoid these uncertainties it is necessary to carry out studies on systems offering the dissociation process as isolated as possible from further processes, preferably as the only process occurring.

Our studies on the dynamic behavior of some Pd and Pt organometallic compounds of the type $[M(C_6F_5)X$. $(EPPy_nPh_{3-n})]$ (M = Pd, Pt; X = C_6F_5, halide; E = O, S; n = 1, 2, 3; Py = pyridin-2-yl) have given us the opportunity to (i) observe dissociative processes involving either halide or a neutral ligand, as well as associative processes, not followed by further transformations; (ii) evaluate the corresponding activation parameters; and (iii) compare identical Pd and Pt systems in substitution reactions. This first paper deals with complexes of the type $[Pd(C_6F_5)X(SPPy_nPh_{3-n})]$ (X = Br for n = 1, 2, 3; X = Cl, I for n = 2), and proves that rotation of the C_6F_5 group is severely hindered in the square-planar complexes but occurs easily in a threecoordinate intermediate produced by halide dissociation.

Results and Discussion

A. Synthesis and Characterization of the Complexes in the Solid State. The complexes [Pd- $(C_6F_5)Br(SPPy_nPh_{3-n})$] (n = 1 (1), 2 (2b), and 3 (3)) were synthesized by reacting $[Pd(C_6F_5)Br(NCMe)_2]$ or (N-Bu₄)₂[Pd₂(μ -Br)₂(C_6F_5)₂Br₂] with a slight excess of the



Figure 2. ORTEP drawing of the complex $[Pd(C_6-F_5)Br(SPPy_2Ph)]$ (2b), with the labeling scheme indicated. Atoms are represented by their 50% probability elipsoids.

corresponding $SPPy_nPh_{3-n}$ ligand (eq 1). The chloro (2a)

$$(NBu_4)_2[Pd_2(\mu-Br)_2(C_6F_5)_2Br_2] + 2 SPPy_nPh_{3-n} \rightarrow 2[Pd(C_6F_5)Br(SPPy_nPh_{3-n})] + 2(NBu_4)Br (1)$$

and iodo (2c) derivatives with SPPy₂Ph were obtained by metathetical reactions in acetone from 2b and AgCl or KI, respectively.

The solid state IR spectra of all the complexes show the $\nu(P=S)$ absorption at 620–625 cm⁻¹, i.e., shifted 25– 35 cm⁻¹ downwards compared to the free ligand. This supports that, at least in the solid state, the ligands SPPy_nPh_{3-n} are acting as S,N-chelates (Figure 1).

The molecular structure of **2b** was studied by X-ray diffraction, and an ORTEP drawing of the molecule is shown in Figure 2 (note that the atom labeling in Figure 2 holds only for the X-ray data description and tables, whereas a chemical labeling will be used for the rest of the discussion, as defined at the beginning of section B). The bond distances and angles observed (Table 1) can be considered as normal. The palladium atom has an essentially square-planar geometry, and the neutral ligand is acting as S,N-chelate, as expected. The fivemembered metallacycle is not planar: C1 and P are respectively 0.4814(55) and 0.9642(16) Å above the mean coordination plane containing Pd, Br, S, N1, and C17. The C_6F_5 group is *cis* to the sulfur atom (in agreement with the expected antisymbiotic behavior of palladium)⁹ and lies roughly perpendicular to the

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Table 1. Selected Bond Distances and Angles and Their Estimated Standard Deviations for $[Pd(C_6F_5)Br(SPPy_2Ph-N,S)]$ (2b)

Distances, Å				
Pd-Br	2.425(1)	$\dot{C}(3) - C(4)$	1.37(2)	
Pd-S	2.307(2)	C(4) - C(5)	1.37(1)	
Pd - N(1)	2.141(5)	C(6) - C(7)	1.364(9)	
Pd - C(17)	1.978(7)	C(7) - C(8)	1.40(1)	
S-P	1 991(2)	C(8) - C(9)	1.36(1)	
$\vec{\mathbf{P}} - \mathbf{C}(1)$	1.801(6)	C(9) - C(10)	1.36(1)	
$\mathbf{P} - \mathbf{C}(\mathbf{G})$	1.811(6)	C(11) - C(12)	1 384(9)	
P = C(11)	1.704(6)	C(11) = C(12)	1 389(0)	
F = O(11) F(1) = O(19)	1.734(0)	C(11) = C(10) C(12) = C(12)	1.002(3) 1.97(9)	
F(1) = C(10) F(0) = C(10)	1.040(9)	C(12) = C(13) C(12) = C(14)	1.37(2) 1.90(1)	
F(2) = C(19) F(2) = C(20)	1.338(9)	C(13) = C(14)	1.09(1)	
F(3) = C(20)	1.34(1)	C(14) = C(15)	1.30(1)	
F(4) = C(21)	1.337(8)	C(15) = C(16)	1.38(2)	
F(5) - C(22)	1.349(7)	C(17) - C(18)	1.36(1)	
N(1) - C(1)	1.340(8)	C(17) - C(22)	1.363(9)	
N(1) - C(5)	1.344(8)	C(18) - C(19)	1.37(1)	
N(2) - C(6)	1.336(8)	C(19) - C(20)	1.35(1)	
N(2) - C(10)	1.336(9)	C(20) - C(21)	1.36(2)	
C(1) - C(2)	1.377(9)	C(21) - C(22)	1.374(9)	
C(2) - C(3)	1.39(1)			
	A			
	Angi	es, aeg	110.0(7)	
Br-Pa-S	175.23(5)	C(8) = C(9) = C(10)	119.8(7)	
Br-Pd-N(1)	94.3(1)	N(2) - C(10) - C(9)	123.2(7)	
Br-Pd-C(17)	86.4(2)	P - C(11) - C(12)	118.0(5)	
S-Pd-N(1)	89.9(1)	P-C(11)-C(16)	122.0(5)	
S-Pd-C(17)	89.7(2)	C(12)-C(11)-C(16)	120.0(6)	
N(1) - Pd - C(17)	176.8(2)	C(11)-C(12)-C(13)	119.8(6)	
Pd-S-P	94.23(8)	C(12)-C(13)-C(14)	119.9(7)	
S-P-C(1)	107.6(2)	C(13)-C(14)-C(15)	1 19.9 (7)	
S-P-C(6)	113.7(3)	C(14)-C(15)-C(16)	121.4(7)	
S - P - C(11)	112.3(3)	C(11)-C(16)-C(15)	119.0(6)	
C(1) - P - C(6)	106.4(3)	Pd-C(17)-C(18)	124.7(5)	
C(1) - P - C(11)	107.8(3)	Pd-C(17)-C(22)	121.4(5)	
C(6) - P - C(11)	108.9(3)	C(18)-C(17)-C(22)	113.9(6)	
Pd - N(1) - C(1)	118.6(4)	F(1)-C(18)-C(17)	119.3(7)	
Pd - N(1) - C(5)	123.3(4)	F(1)-C(18)-C(19)	116.8(6)	
C(1) - N(1) - C(5)	118.2(5)	C(17) - C(18) - C(19)	123.8(7)	
C(6) - N(2) - C(10)	116.5(6)	F(2) - C(19) - C(18)	120.7(7)	
P - C(1) - N(1)	115.9(4)	F(2) - C(19) - C(20)	120.0(7)	
P - C(1) - C(2)	121.7(5)	C(18) - C(19) - C(20)	1194(7)	
N(1) = C(1) = C(2)	122.1(0) 122 $4(6)$	F(3) = C(20) = C(19)	120.0(7)	
C(1) = C(2) = C(3)	118 6(6)	F(3) - C(20) - C(21)	119.8(7)	
C(1) = C(2) = C(3)	110.0(0) 110.0(7)	C(10) = C(20) = C(21)	120.2(8)	
C(2) = C(3) = C(4) C(3) = C(4) = C(5)	110.9(2)	F(4) = C(21) = C(21)	110 9(6)	
U(3) = U(4) = U(3) N(1) = O(5) = O(4)	100 4(6)	F(4) = O(21) = O(20) F(4) = O(21) = O(20)	199.9(7)	
$\mathbf{N}(1) = \mathbf{U}(0) = \mathbf{U}(4)$ $\mathbf{D} = \mathbf{U}(0) = \mathbf{N}(0)$	112 9(4)	$\Gamma(4) = O(21) = O(22)$ O(20) = O(21) = O(22)	122.2(7)	
$\mathbf{r} = \mathbf{O}(0) = \mathbf{N}(\mathbf{Z})$	113.3(4)	E(20) = U(21) = U(22)	110.1(7)	
$\mathbf{F} = \mathbf{C}(\mathbf{b}) = \mathbf{C}(7)$	122.5(4)	F(5) = U(22) = U(17) F(5) = O(22) = O(21)	115.8(6)	
N(2) = C(6) = C(7)	124.1(6)	F(5) = U(22) = U(21)	115.5(6)	
C(6) = C(7) = C(8)	117.6(6)	C(17) - C(22) - C(21)	124.7(7)	
C(7) - C(8) - C(9)	118.8(6)			

coordination plane (dihedral angle $98.64(18)^\circ$). The coordinated Py ring makes a dihedral angle of 20.84-(36)° with the coordination plane. The N atom of the noncoordinated Py group is away from the metal.

B. Solution Behavior of the Complexes. The complexes have been studied in CDCl_3 and acetone- d_6 solution by ¹H, ³¹P, and ¹⁹F NMR spectroscopies (Table 2). The latter is particularly clear and informative: The number of F_{para} (F⁴) signals reveals the number of isomers in solution, whereas the F_{ortho} signals (F² and F⁶) report on the equivalence or inequivalence of the two halves of a given C_6F_5 group (Figure 1).^{10,11} In the ¹H NMR spectra the chemical shift of H⁶ (the H atom on C⁶ in the Py groups) is very sensitive to the coordinated or noncoordinated nature of the group and, when coordinated, to the *cis* ligand.¹²



B.1. Complex 1. Complex 1 (Figure 1, $R^1 = R^2 =$ Ph) shows only one isomer both in CDCl₃ and in acetone d_6 . The chemical shift of H⁶ (δ (H⁶) = 9.78 ppm) is similar to that found for the coordinated Py in complex **2b.1** (see below and Scheme 1); hence, this group in 1 must be also *cis* to Br. In a rigid structure for 1, identical to that found for complex 2b in the solid, the two halves of the C_6F_5 ring should be strictly inequivalent, but they appear as equivalent in the ¹⁹F spectrum at all temperatures, both in $CDCl_3$ and in acetone- d_6 . This equivalence can be achieved by either of the two following processes: (a) Rotation of the C_6F_5 ring, which can be discounted because it should be slow in CDCl₃ (see below, discussion for complexes 2); and (b) a fast envelope-shift movement taking C² and P up and down the coordination plane, as represented in Figure 1, which must be the process operating. This allows us to continue the rest of the discussion as if the fivemembered metallacycle defined by the N,S-chelating ligand was planar.

B.2. Complexes 2a, 2b, and 2c. Possible species and mechanisms operating for these complexes are depicted in Scheme 1. The ¹⁹F, ¹H, and ³¹P NMR spectra of complex 2b in CDCl₃ at room temperature show the presence of two isomers. The ¹H spectrum of the major isomer (2b.1, >95%) displays the signals expected for two inequivalent Py groups: one noncoordinated ($\delta(H^6) = 8.82$ ppm) and the other coordinated *cis* to Br ($\delta(H^6) = 9.81$ ppm), as found in the X-ray structure determination. In the ¹⁹F spectrum (Figure

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Table 2. Relevant ³¹ P, ¹ H, and ¹⁹ F NMR Data for the Complexes ^{a}						
complex	\mathbf{P}^{b}	${ m H}^6 { m Py}_{ m coor}{ m ^c}$	H ⁶ Py _{free} ^c	F^{6} and F^{2} or F^{6} + F^{2} c	F ⁵ and F ³ or F ⁵ + F ³ ^c	F ⁴ d
1	52.6	9.74		-118.4	-164.6	-161.5
2a.1	46.9	9.62	8.82	-118.7, -119.5	-164.0	-160.8
2a.2		9.75		-118.2, -122.3	-162.8, -163.2	-160.2
2b.1	45.9	9.81	8.82	-118.1, -118.9	-164.1	-161.0
2b.2		9.73, 8.36		-117.7, -121.4	-162.9, -173.8	-160.1
$2b.1^e$		9.72	8.90	-113.2	-161.7	-158.6
$2\mathbf{b}.2^e$		9.64, 8.47		-111.5, -116.0	-160.5, -161.4	-158.3
2c.1	43.5	10.02	8.81	-115.9, -116.5	-164.4	-161.0
2c.2		9.95		-114.6, -118.5	-163.2, -163.8	-160.1
3.1	42.3	9.09	8.90	-118.7	-163.1	-159.9
3.2	39.5	9.73, 8.40	8.94	-119.5, -122.0	-161.7, -162.4	-159.2

^a All data at 294 K, except **3.2** at 213 K. In CDCl₃ unless otherwise stated. ^b Singlet. ^c Multiplet. ^d Triplet. ^e In acetone-d₆.



-120 -160 -165 Ppm -115 Figure 3. ¹⁹F NMR spectrum of [Pd(C₆F₅)Br(SPPy₂Ph)]

(2b) at 294 K in CDCl₃ (a) and in acetone- d_6 (b).

3a) the five fluorine atoms of this isomer give rise to five signals, i.e., the two halves of the C_6F_5 ring appear as inequivalent. This result would indicate a rigid structure in which the C_6F_5 group is not rotating around the Pd-C bond; in fact a slow rotation is taking place, as discussed later. The minor isomer also shows inequivalence for the two halves of the C_6F_5 ring, and the signals observed in the ¹H and ¹⁹F spectra suggest for it structure **2b.2**, in which the neutral ligand is acting as a N,N-chelate. This is the kind of structure found for the corresponding complex with OPPy₂Ph and is not considered in detail here as it will be discussed in a forthcoming paper on $OPPy_nPh_{3-n}$ complexes.

In acetone- d_6 , the NMR spectra of complex **2b** show again the presence of two isomers (Figure 3b), but now the ¹⁹F spectrum of the major isomer **2b.1** shows only three signals (2:1:2), i.e., the two halves of the C_6F_5 ring appear as equivalent, even at 213 K. Meanwhile, its ¹H spectrum shows the two Py groups to be still inequivalent, one noncoordinated and the other coordinated cis to Br. Hence, the mechanism producing equivalence of the two halves of the C_6F_5 ring does not involve exchange of free and coordinated Py groups (i.e., equilibrium ii in Scheme 1 is very slow). In addition, the signals of the second and very minor isomer are still observed, thus excluding any process going via the N,Nchelated structure (i.e., equilibrium i in Scheme 1 is also very slow; its rate is measured later for the related complex 3).

This led us to C_6F_5 rotation as the mechanism producing equivalence, and we must address the question whether this rotation occurs (a) directly on the square-planar complex 2b.1 (path iii); (b) via an associative process on the pentacoordinate intermediate (not depicted in Scheme 1); or (c) via a dissociative process, on a three-coordinate intermediate (such as 2b.3 in Scheme 1, path iv).

The first possibility, rotation directly on **2b.1**, can be discounted because (1) the solvent should not have a marked effect on the rate of rotation, whereas the observed behavior is fast rotation in acetone- d_6 and slow rotation in $CDCl_3$ (see below, kinetic experiments); and (2) the rotation in the square-planar complex looks severely hindered sterically. In effect, by applying the data found in the X-ray determination of 2b to a rotamer in which the C_6F_5 ring becomes coplanar with the coordination plane (Figure 4), a very short distance (202 pm) is calculated between the ortho fluorines and the coordinated Br and S atoms. This distance means a contraction to about 62% of the sum of the van der Waals radii (330 and 320 pm, respectively),¹³ which seems unacceptable. To avoid this the complex should undergo severe distortions at this stage of rotation,

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Figure 4. Chart of a hypothetical square-planar rotamer with the C_6F_5 ring coplanar with the coordination plane.

implying a very high activation energy for the rotation.¹⁴ As a matter of fact, our results discussed below mean that the most accessible distortion turns out to be the heterolytic cleavage of the Pd-Br bond.

The second possibility, an associative mechanism involving coordination of the solvent, would be consistent with the acceleration of rate observed in acetone, but it is not clear whether the C_6F_5 rotation should be less hindered in a five-coordinate intermediate than in a square-planar complex. Moreover, it is difficult to understand why in the absence of a coordinating solvent (CDCl₃) this mechanism should not be triggered by the pendant Py group.

The third possibility, a dissociative mechanism, might involve Pd–S or Pd–Br dissociation, both facilitating equally the C_6F_5 rotation. The former can be discounted because it should not be so very sensitive to a change of solvent and, more importantly, because it should predictably trigger simultaneously equilibrium i, which is not observed. Dissociation of anionic Br⁻ might explain the acceleration observed in acetone, a more polar solvent with a higher dielectric constant than chloroform.

Overall, qualitative considerations seem to favor $Br^$ dissociation, but kinetic studies are needed to substantiate any decision between the associative and and the dissociative path.

Kinetic Studies. The C_6F_5 rotation for $[Pd(C_6F_5)-Br(SPPy_2Ph-N,S)]$ in acetone- d_6 is fast (see Figure 3b and ref 30). In CDCl₃, the ¹⁹F spectra show the molecule as apparently rigid (Figure 3a, F² and F⁶ inequivalent) in the range of temperatures accessible, but magnetization transfer experiments on the F_{ortho} signals confirm that a slow rotation exchanging F² and F⁶ is occurring and allow kinetic studies to be undertaken (Figure 5). In this way the rotation rate constants can be evaluated from the experimental magnetization transfer constants as $k_{\rm rot} = 2k_{\rm MT}(F^2 \rightarrow F^6).^{15}$

(i) Influence of the Halide. The temperature dependence of the rotation rate was determined for [Pd-

Table 3. Temperature Dependence of C_6F_5 Rotation Rate in Complexes 2a.1, 2b.1, and 2c.1 in CDCl₃ (k_{rot} in s⁻¹)

$k_{ m rot}({f 2a.1})/T({ m K})$	$k_{ m rot}({ m 2b.1})/T{ m (K)}$	$k_{ m rot}({ m 2c.1})/{T m (K)}$
1.41/291.6	3.54/291.6	2.13/269.8
2.23/296.6	6.33/296.6	4.49/276.3
3.74/302.5	9.81/302.6	6.93/283.5
7.59/311.5	16.68/311.5	12.09/289.9
12.52/317.5	29.32/317.0	22.47/299.6
17.01/323.2	41.72/323.2	38.89/306.6

Table 4. Activation Parameters for C₆F₅ Rotation in [Pd(C₆F₅)X(SPPy₂Ph-N,S)] (2b.1) in CDCl₃ (Standard Deviations in Parentheses)

X	Cl	Br	I
$\begin{array}{l} \Delta H^{\sharp} (\mathrm{kJ \ mol^{-1}}) \\ \Delta S^{\sharp} (\mathrm{J \ K^{-1} \ mol^{-1}}) \end{array}$	60.0(1.2) -35.8(3.9)	57.1(2.5) - 37.5(8.2)	50.2(0.6) -51.1(2.0)

Table 5. Thermodynamic Differences for Cl, Br, and I Involved in a Heterolytic Cleavage $[Pd-X] \rightarrow [Pd]^+ + X^{-a}$

X–X′	$\Delta_D(Pt)$	$\Delta_{\rm EA}$	$\Delta_{\rm free}$	Δ_{exp}	$\Delta_{ ext{hydr}}$	$\Delta_{ m solv}$
Cl-Br Br-I Cl-I	$33.5 \\ 48.5 \\ 82.0$	-24.4 -29.4 -53.8	9.1 19.9 28.2	2.9 6.9 9.8	$-31.35 \\ -40.96 \\ -72.31$	-22.25 -21.86 -44.11

^{*a*} In kJ mol⁻¹; Δ taken as {(value for X) - (value for X')}.

 $(C_6F_5)Br(SPPy_2Ph-N,S)]$ (2b) and for their Cl (2a) and I (2c) derivatives, Table 3). The Eyring plots in Figure 6 yield the activation parameters in Table 4. A decrease in ΔH^{\dagger} is observed in the sequence Cl > Br > I. Again this trend discounts rotation directly in the fourcoordinate species 2b.1, where the bulkiest halogen atom should produce the biggest hindrance and the highest ΔH^{\dagger} . Furthermore, it supports the notion that rotation is preceded by halide dissociation, which we believe should be easiest for the heaviest halogen. The sequence of lability observed, Cl < Br < I is in contrast to that observed for the isomerization of cis-[Pt(YC₆H₄)X- $(PEt_3)_2$] in methanol, which occurs via dissociative loss of the X⁻ ligand.¹⁶ In that work the sequence of lability, Cl > Br > I, is said to reflect a variation of the bond strength of the halide ions to the "soft" metal center in the order Cl < Br < I, but there is much evidence against this affirmation. It is rather general that M-X dissociation energies for transition metals follow the order Cl > Br > I.¹⁷ For a heterolytic cleavage a rough calculation of the differences for the three halides is given in Table 5, along with the parameters involved. The differences in bond dissociation energy (Δ_D) for Pt (as the element closest to Pd for which we have found data) are taken¹⁸ and are corrected for the differences in electron affinity of the halogens (Δ_{EA}) .¹⁹ This provides the difference in energy (Δ_{free}) for the formation of well-separated unsolvated ion pairs (i.e., assuming equal electrostatic energy for the three anions), which is unfavorable for the dissociation of Cl⁻ by about 9 kJ mol⁻¹ as compared to Br⁻ and by 28 kJ mol⁻¹ as compared to I⁻ (the experimental differences in activa-

⁽¹⁴⁾ Examples of restriction to rotation in aryl derivatives are not uncommon. See, for instance: (a) Alcok, W.; Brown, J. M.; Pérez-Torrente, J. Tetrahedron Lett. **1992**, 33, 389. (b) Alsters, P. L.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. Organometallics **1993**, 12, 1639. (c) Wada, M.; Sameshima, K. J. Chem. Soc., Dalton Trans. **1981**, 240. (d) Baumgärtner, R.; Brune, H. A. J. Organomet. Chem. **1988**, 350, 115. (e) Anderson, G. K.; Cross, R. J.; Manojlovic-Muir, L.; Muri, K. W.; Rocamora, M. Organometallics **1988**, 7, 1520.

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⁽¹⁹⁾ Huheey, J. E.; Keiter, E. A.; Keiter, R. L. Inorganic Chemistry. Principles of Structure and Reactivity, 4th ed; Harper Collins College Publishers: New York, 1993; p 43.



Figure 5. Plot of magnetization transfer, $F^2 \rightarrow F^6$.



Figure 6. Eyring plots of k_{rot} of C_6F_5 for the compounds $[Pd(C_6F_5)X(SPPy_2Ph)]$ (X = Cl, 2a; Br, 2b; I, 2c).

tion enthalpy, Δ_{exp} , are 2.9 and 9.8, respectively). If the heterolytic cleavage occurs in the presence of a solvating solvent, then the differences in solvation energies for the three anions (for a common cation) have to be considered. These can be rather high and overcome the previous differences, as is the case with hydration energies (Δ_{hydr}).^{20,21} The heterolytic cleavage of the hydrated ions (estimated as $\Delta_{solv} = \Delta_{free} + \Delta_{hydr}$) is favorable for the dissociation of Cl⁻ by about 22 kJ mol⁻¹ as compared to Br⁻, and by 44 kJ mol⁻¹ as compared to I⁻. Still making the reasonable assumption that the order of stabilities in the rate-determining transition state is the same as for the dissociated systems one can be rather sure, even at this very crude level of approximation, that the order of lability toward heterolytic dissociation, Cl < Br < I, found in this paper in the nonsolvating $CDCl_3$, reflects the relative bond strength of the three "soft" halide ions to the "soft" Pd center; the inverse order found previously for cis-[Pt(YC₆H₄)X-(PEt₃)₂] was deduced from kinetic studies in MeOH and reflects the very important contribution of the solvation energies, not the bond strengths.

The negative values of ΔS^{\dagger} found in our system do not contradict a dissociative process in solution. For instance, the DMSO exchange in $[PtPh_2(Me_2SO)_2]$, which is undoubtedly dissociative ($\Delta V^{\dagger} = +4.9 \pm 0.5 \text{ cm}^3$ mol⁻¹),^{2a} shows a $\Delta S^{\ddagger} = -16 \pm 2$ cal K⁻¹ mol⁻¹.^{2b} The dissociation of the halo ligand in our system produces a tight ion pair in a cage of solvent (see next section); hence, the leaving group is not very much loosened in the transition state and a large positive ΔS^{\dagger} is not to be expected. In addition, some $Pd \cdots F_{ortho}$ interaction in the transition state, assisting the dissociation, might reduce the rotational entropy. On the other hand, the ion pair must induce some solvent ordering in the transition state, leading to a negative contribution to ΔS^{*} . Altogether, the positive contributions to ΔS^{*} are expected to be small and can be compensated by the negative contributions.

(ii) Salt Effects. The effect of adding $(n-Bu_4N)Br$ or $(n-Bu_4N)ClO_4$ on the rotation rate of $[Pd(C_6F_5)-Br(SPPy_2Ph-N,S)]$ in CDCl₃ (Table 6) is shown in Figure 7. Both salts produce a moderate acceleration effect which is more pronounced at the initial stage and somewhat stronger for $(n-Bu_4N)ClO_4$. The meaning of these results needs to be considered very cautiously: Compared to the many studies on the effect of added salts on reaction rates in polar and dissociating solvents,²²⁻²⁴ salt effects in nonpolar solvents have been little studied. Kinetic studies in nonpoar solvents are complicated by the nonideal nature of solutions of ionic

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⁽²¹⁾ Duncan, A.; Pople, J. Trans. Faraday Soc. 1953, 49, 217.

Table 6. Salt Effects on the C_6F_5 Rotation Rate in Complex 2b.1 in $CDCl_3^a$

$[(NBu_4)ClO_4]/k_{rot}$	[(NBu ₄)ClO ₄]/k _{rot}
0.000/2.70	0.000/2.70
0.020/3.20	0.029/3.73
0.064/3.58	0.087/4.30
0.128/3.79	0.174/4.92
0.300/4.39	0.289/5.31

^{*a*} Salt concentration in mol L⁻¹; k_{rot} in s⁻¹.



Figure 7. Plot of $\ln(k_X/k_0)$ versus c (c = concentration of $(NBu_4)ClO_4$ or $(NBu_4)Br$.

species and the possible aggregation of reactants and products.^{25,26} This must be particularly true for a very poorly dissociating solvent with a low dipole moment, such as CDCl₃ ($\epsilon_r = 4.80$, $\mu = 1.04$ for CHCl₃)²⁷ and highly concentrated solutions (obliged by the use of NMR spectroscopy for the kinetic studies).

The possible steps to be considered in the dissociation of the Pd-Br bond are shown in eqs 2-5: heterolytic cleavage of the Pd-Br bond to give contact ion pairs in a cage of solvent (eq 2); formation of solvent-separated ion pairs (eq 3); exchange reaction between ion pairs (eq 4 for the perchlorate salt or eq 4' for the bromide salt); and complete ion dissociation (eq 5). In the event of an associative mechanism (unlikely with the information already discussed) we should also consider anion coordination with formation of a pentacoordinate species in which (supposedly) the C_6F_5 rotation should occur more easily (eq 6).

For an associative mechanism (eq 6) an accelerating effect can be expected for the bromide but not for the perchlorate salt;²⁸ thus, the observation of a larger effect for perchlorate is evidence against the operation of an associative mechanism. On the other hand, the difference between the effects of the two salts is quantitatively small. This is the kind of behavior expected for nonpolar solvents in which the salts are present as ion pairs or higher aggregates (i.e., in which eqs 3, 4, and 5 are not operating). 25,26,29

$$(L-L')(C_6F_5)PdBr\frac{k_1}{k_{-1}}(L-L')(C_6F_5)Pd^+Br^-$$
 (2)

$$(L-L')(C_6F_5)Pd^+, Br^- \neq (L-L')(C_6F_5)Pd^+||Br^-||$$
 (3)

$$(L-L')(C_6F_5)Pd^+||Br^- + ClO_4^-||NBu_4^+ \Leftrightarrow$$

 $(L-L')(C_6F_5)Pd^+||ClO_4^- + Br^-||NBu_4^+ (4)$

$$\begin{aligned} (L-L')(C_6F_5)Pd^+ ||Br^- + *Br^-||NBu_4^+ \rightleftharpoons \\ (L-L')(C_6F_5)Pd^+ ||*Br^- + Br^-||NBu_4^+ (4') \end{aligned}$$

$$(L-L')(C_6F_5)Pd^+||Br^- \stackrel{solv}{\Longrightarrow} [(L-L')(C_6F_5)Pd^+]_{solv} + [Br^-]_{solv} (5)$$

$$[Pd(C_6F_5)Br(L-L')] + (NBu_4)X \rightleftharpoons$$
$$[PdX(C_6F_5)Br(L-L')]^- + NBu_4^+ (6)$$

Consequently, the evidence points to rotation in a three-coordinate cation 2b.3 (Scheme 1) forming part of a contact ion pair in a cage of solvent (eq 2). This agrees with the simple model proposed by Perrin and Pressing for salt effects in less polar solvents. In this model the transition state (in a vanishingly small concentration) is a dipole rather than an ion, and the added salts are also present as ion pairs or higher aggregates. The effect of these dipolar interactions for a single added salt and low salt concentrations should obey eq 7, where b can be calculated (b_{calcd} for Bu₄NClO₄ $= 6.8; b_{calcd} \text{ for } Bu_4 NBr = 4.3).^{29}$

$$\ln \frac{k}{k_0} = b[\text{salt}] \tag{7}$$

$$\frac{\ln[k(\text{ClO}_4^{-})/k_0]}{\ln[k(\text{Br}^{-})/k_0]} = \frac{b_{\text{calcd}} \text{ (for NBu}_4\text{ClO}_4)}{b_{\text{calcd}} \text{ (for NBu}_4\text{Br})} = 1.58 \quad (8)$$

The ratio of salt effects for the two salts at the same concentration should be 1.58, according to eq 8. It is remarkable that, even though the concentrations used in this work are high, the ratio of the effects produced by the two salts is in the range 1.6-1.4, as can be seen in Figure 7.

Our results illustrate clearly the enormous changes in salt effects when nondissociating solvents are used. Thus the effect of addition of a common ion salt on a dissociative process is not a retardation of rate by the common ion mass effect, as in dissociating solvents. Rather to the contrary, an acceleration is produced as a consequence of the stabilization of the dipolar transition state in the increasingly polar atmosphere produced by the increasing concentration of dipoles or multipoles of the added salt in the nonpolar solvent.

Figure 8 shows a pictorial model of the concerted C_6F_5 rotation in CDCl₃ according to the evidence discussed. In each half rotation the C_6F_5 group will "push" the dissociated halide away from its coordination site, but not very far away since this is happening in a cage of solvent. It is a reasonable speculation that the halide

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(25) Smith, P. J.; Wilcox, C. S. J. Org. Chem. 1990, 55, 5675 and

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Am. Chem. Soc. 1985, 107, 1. (28) See, for example: Hansson, S.; Norrby, P.-O.; Sjögren, P. T.;

Akermark, B.; Cucciolito, M. E.; Giordano, F.; Vitagliano, A. Organometallics 1993, 12, 4940.

⁽²⁹⁾ Perrin, C. L.; Pressing, J. J. Am. Chem. Soc. 1971, 93, 5705.



Figure 8. Space-filling model for the C_6F_5 rotation in $[Pd(C_6F_5)Br(SPPy_2Ph)]$ (**2b**) in CDCl₃; the molecule is viewed along the bisectrix of the Br-Pd-C angle, and the labels refer to Scheme 1.

will move to some location over the coordination square plane where the anion-cation distance can be shorter and the electrostatic interactions can be higher and will fall back to its coordination site as soon as it is available. In dissociating solvents (e.g., acetone), separated solvated ions will be produced (eq 5). In other words, the halide is engaged or declutched from the rotor depending on the environment, the dissociating solvents letting out the clutch to allow faster rotation of the C_6F_5 group.^{30,31}

B.3. Complex 3. The species and mechanisms operating for complex 3 are shown in Scheme 2. The solubility of the compound in acetone is very low, and studies could be carried out only in CDCl₃. Two isomers are observed: the N,S-chelate 3.1 and the N,N-chelate 3.2 in an approximate 3:2 ratio at 298 K. The increase in proportion of the N.N-chelate isomer in 3 as compared to complex **2b** is very much higher than the factor of 2 expected from the higher effective concentration of the Py group in the former.³² Two plausible explanations are a decrease in nucleophilicity of the sulfur atom in SPPy₃ induced by the higher electron-attracting ability of the Py groups compared to the Ph groups or a weak bonding interaction of the third Py group to Pd (in a square-pyramidal geometry), since we observe three inequivalent Py groups at low temperature.³³

The equilibrium 3.1 \leftrightarrow 3.2 is slow ($k_1 = 0.33 \text{ s}^{-1}$; $k_{-1} = 0.52 \text{ s}^{-1}$, measured by magnetization transfer experi-



ments on the ³¹P signals at 298 K). F^2 and F^6 in 3.1 are inequivalent at room temperature; slow C_6F_5 rotation in 3.1 via Br⁻ dissociation should be occurring, as in 2b.1, but this was not studied. In isomer 3.2, F^2 and F^6 are equivalent at room temperature but become inequivalent at low temperature (coalescence temperature = 243 K at 75 MHz; $\Delta G^4 = 44.25$ kJ mol⁻¹). This apparent C_6F_5 rotation is in reality a consequence of exchange of the uncoordinated Py group and the Py group *trans* to the Pd-C bond (N¹ and N³ in Scheme 2). This can be clearly seen in the ¹H spectra in Figure 9 that show exchange of H⁶ signals between only two Py groups. Detailed studies on related complexes with OPPy₃, to be presented in a forthcoming paper, support an associative mechanism for this process.

Conclusion

The rotation of the C_6F_5 group around the Pd-C bond in complexes $[Pd(C_6F_5)X(SPPy_nPh_{3-n}-N,S)]$ in CDCl₃ involves a simple halide dissociation not followed by any subsequent process except the rotation itself. The

⁽³⁰⁾ Coalescence in acetone- d_6 is observed at 228 ± 15 K (a more precise value is difficult to assign due to the proximity of the signals) for the signals of F³ and F⁵, for which the chemical shift difference below coalescence is $\delta v = 83.9$ Hz. Then, applying the equation for the coalescence temperature $k = 2\pi\delta v/\sqrt{2}$, a value of $k_{\rm rot}$ (chloride in acetone) = 186 s⁻¹ at T = 228 K is obtained. This can be compared with the value calculated from the Eyring plots for the rotation in chloroform, $k_{\rm rot}$ (chloride in chloroform) = 8.94×10^{-3} s⁻¹ at T = 228 K. Hence, the rotation is about 20 000 times faster in acetone than in chloroform. Possibly in acetone the transient species [Pd(C₆F₅)(SPPy_2Ph-N,S)(acetone)]⁺X⁻ are formed, and the fast rotation indicates that decoordination of the hard ligand acetone from [Pd(C₆F₅)(SPPy_2Ph-N,S)(acetone)]⁺ is very easy.

⁽³¹⁾ Molecular motors and brakes are fashionable nowadays (see, for instance: (a) Kelly, T. R.; Bowyer, M. C.; Bhaskar, K. V.; Bebbington, D.; García, A.; Lang, F.; Kim, M. H.; Jette, M. P. J. Am. Chem. Soc. 1994, 116, 3657. (b) Fanizzi, F. P.; Lanfranchi, M.; Natile, G.; Tirpicchio, A. Inorg. Chem. 1994, 33, 3331). Ours offers the novelty that, in CDCl₃, the dissociated halide should show marked preference for one of the two faces of the coordination plane (either the Py side or the Ph side), thus producing a preferable "sense" for the ionization in each enantiomer (our compound is a racemic mixture). The rotation itself converts degenerate states and cannot have a preferred sense, according to the microscopic reversibility principle.

⁽³²⁾ Carter, M. J.; Beattie, J. K. Inorg. Chem. 1970, 9, 1233.

⁽³³⁾ We consider this latter possibility unlikely. In Pt, which shows a much greater tendency to pentacoordination than Pd, good N-donor ligands (ours is weak) and some π -acceptor ancillary ligand are necessary to promote five-coordination. Moreover, with trispyrazolylborates the resulting geometry is bipyramidal with two equatorial (hence equivalent) pyrazolyl groups. See, for instance: Albano, V. G.; Demartin, F.; De Renzi, A.; Morelli, G.; Saporito, A. *Inorg. Chem.* **1985**, 24, 2032 and references therein.



Figure 9. ¹H NMR spectrum of $[Pd(C_6F_5)Br(SPPy_3)]$ (3) at the temperatures indicated. Lables refer to the H⁶ atom of each Py ring in Scheme 2. For instance, 2 stands for H⁶ in the Py ring containing N².

rotation occurs in a contact ion pair in a cage of solvent, $[Pd(C_6F_5)(SPPy_nPh_{3-n})]^+X^-$. The fact that the rotation is very fast in acetone shows that the rotation itself has a low activation energy. Hence the enthalpy values observed for the slow rotation in CDCl₃ must correspond closely to the dissociation. The activation enthalpies decrease in the order Cl > Br > I, reflecting the decreasing affinity of the three "soft" halides for the "soft" palladium(II) in the absence of important solvation effects. The activation entropies for these dissociative processes in CDCl₃ are negative.

Experimental Section

General Methods. C, H, and N analyses were carried out on a Perkin-Elmer 240 microanalyzer. IR spectra were recorded (in the range 4000-200 cm⁻¹) on a Perkin-Elmer 883 spectrometer. $[Pd(C_6F_5)_2(NCMe)_2]^{10}$ and $(NBu_4)_2[Pd_2(\mu-Br)_2 (C_6F_5)_2Br_2]^{34}$ were prepared as described elsewhere. The phosphines³⁵ and their sulfides³⁶ were made by methods in the literature.

NMR Measurements. NMR spectra were recorded on a Bruker AC300 spectrometer with a thermostated multinuclear QNP probehead operating in the FT mode at 300 MHz (¹H),

Table 7.	Selected Cr	ystal and	Refinement	Data
for	$[Pd(C_6F_5)Br($	SPPy ₂ Ph	-N.S] (2b.1)	

	<u>yzi ii</u> (1001)
formula	$C_{22}H_{13}BrF_5N_2PPdS$
$M_{\rm r}$	649.70
cryst syst	monoclinic
space group	$P2_1/c$
$a, \mathrm{\AA}$	8.273(2)
b, Å	14.240(2)
c, Å	19.547(4)
β , deg	95.10(2)
V, Å ³	2293.6(7)
F(000)	1264
Ζ	4
$D_{ m calcd},{ m g/cm^3}$	1.88
μ , cm ⁻¹	27.3
no. of rflns collected	4745
no. of indepndt rflns	3134 (≥3 <i>o</i> (I))
no. of refined params	298
largest peak/hole, e/Å ³	+0.70/-0.65
R^a	0.042
R_{w}^{b}	0.047

^{*a*} $R = \sum [|F_{\rm o}| - |F_{\rm c}|/\sum |F_{\rm o}|]$. ^{*b*} $R_{\rm w} = \sum [w(|F_{\rm o}| - |F_{\rm c}|)^2 / \sum w |F_{\rm o}|^2]^{1/2}$, w $= 1/[\sigma(F_0^2) + (0.010F_0)^2 + 1.000].$

282.38 MHz $({\rm ^{19}F}),$ and 121.44 MHz $({\rm ^{31}P}).~{\rm ^{1}H},~{\rm ^{19}F},$ and ${\rm ^{31}P}$ shifts are reported relative to TMS, CFCl₃, and 85% H₃PO₄ as external standards, respectively. Temperature control of the NMR probe was achieved using a Bruker Cryo Controller. The actual temperature was measured before and after spectral accumulation by replacing the sample with Bruker standard samples of methanol-methanol- d_4 for low temperatures and ethylene glycol in DMSO- d_6 (80/20) for high temperatures and using the equations provided by the manufacturer.

The magnetization transfer measurements were performed using the inversion-recovery technique. Selective inversion of one signal was achieved using the "1, -1" pulse train (90°- D_1-90°); after a variable time t a nonselective 90° pulse allows observation of the signals. Data analysis was carried out as described in the literature.¹⁵ The most popular "1,-3,3,-1" pulse train $(25.5^{\circ}-D_1-67.5^{\circ}-D_1-67.5^{\circ}-D_1-25.5^{\circ})$ gives worse results for our samples; it may be due to the loss of coherence of the components of each multiplet during three D_1 delays. For the magnetization transfer experiments, 4000 data points were recorded over a sweep width of 1795 Hz (0.414 Hz/point) and required 8 scans with a delay between scans of at least $5T_1$. Special care was taken to accurately measure the pulse length for each sample.

The samples for the salt effect studies were prepared as follows: A stock 0.04 M solution of the palladium complex was prepared in deoxygenated CDCl₃. To one aliquot of this solution was added (NBu₄)X (X = ClO_4^{-} , Br⁻) to obtain a solution 0.4 M in the added salt; different salt concentrations were obtained by mixing measured volumes of this solution and of the stock solution.

X-ray Structure Analysis of [Pd(C₆F₅)Br(SPPy₂Ph-**N,S)] (2b).** Recrystallization of $[Pd(C_6F_5)Br(SPPy_2Ph)]$ from CHCl₃ gave a yellow-orange crystal suitable for X-ray diffraction. A total of 4745 independent reflections were measured by $\omega - 2\theta$ scan mode in the range $\theta \leq 26^{\circ}$ (scan rate $16^{\circ} \text{ min}^{-1}$).

The structure was solved by the heavy-atom method and Fourier techniques and refined by the full-matrix least-squares method to final R = 0.042 and $R_w = 0.047$. The highest peak in the final difference Fourier map was of 0.70 e $Å^{-3}$. All H atoms were located theoretically and fixed during the structure refining.

All measurements were made on a Rigaku AFC5R diffractometer at room temperature using Mo Ka ($\lambda = 0.710$ 69 Å) radiation with a graphite monochromator. All calculations were performed on a Micro Vax-II computer using the SDP program package. Details of crystal and refinement data for the structure are given in Table 7. Other pertinent X-ray data are given in the supplementary material.

Preparation of the Complexes. All reactions were carried out under nitrogen atmosphere in deoxegenated solvents.

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⁽³⁶⁾ Mann, F. G.; Watson, J. J. Org. Chem. 1948, 13, 502.

Although the isolated products are stable in the air, the syntheses give some side products and lower yields when an inert atmosphere was not used.

 $[Pd(C_6F_5)Br(SPPyPh_2)] \cdot 0.5OEt_2$ (1). To a solution of $[Pd(C_6F_5)Br(NCMe)_2]$ (0.200 g, 0.463 mmol) in diethyl ether (30 mL) was added SPPyPh₂ (0.1367 g, 0.464 mmol), and the solution was stirred for 15 min. Addition of *n*-hexane (10 mL) and evaporation of the solution to ca. 10 mL produced a yellow solid, which was filtered, washed with *n*-hexane, and air-dried. Yield: 0.239 g, 80%. Calcd: 43.78% C; 2.79% H; 2.04% N. Found: 43.42% C; 2.52% H; 2.02% N.

 $[\mathbf{Pd}(\mathbf{C}_{6}\mathbf{F}_{5})\mathbf{Br}(\mathbf{SPPy_{2}Ph})] (\mathbf{2b}).$ To a solution of $(NBu_{4})_{2}$ - $[Pd_{2}(\mu-Br)_{2}(\mathbf{C}_{6}\mathbf{F}_{5})_{2}Br_{2}] (0.200 \text{ g}, 0.131 \text{ mmol}) \text{ in dichloromethane}$ (30 mL) was added SPPy_2Ph (0.086 g, 0.286 mmol). The solution was stirred for 30 min. Evaporation to a small volume (ca. 10 mL) and addition of ethanol (30 mL) afforded a yellow solid, which was filtered, washed with ethanol, and air-dried. Yield: 0.129 g, 76%. Calcd: 40.73% C; 2.02% H; 4.37% N. Found: 40.98% C; 2.09% H; 4.16% N.

 $[Pd(C_6F_5)Br(SPPy_3)]$, (3) was prepared similarly starting from $(NBu_4)_2[Pd_2(\mu-Br)_2(C_6F_5)_2Br_2]$ (0.200 g, 0.131 mmol) and SPPy₃ (0.080 g, 0.27 mmol). Yield: 0.143 g, 84%. Calcd: 38.79% C; 1.86% H; 6.46% N. Found: 38.91% C; 2.06% H; 6.54% N.

 $[Pd(C_6F_5)Cl(SPPy_2Ph)]$ (2a). To $[Pd(C_6F_5)Br(SPPy_2Ph)]$ (0.150 g, 0.220 mmol) in acetone (50 mL) was added an excess of AgCl, freshly prepared and wet. The mixture was stirred, shielded from light, for 24 h, and the insoluble silver salts were filtered off. Evaporation of the acetone solution and addition of ethanol (10 mL) afforded a pale yellow compound, which was filtered, washed with ethanol, and air-dried. Yield: 0.120 g, 85%. Calcd: 43.66% C; 2.16% H; 4.63% N. Found: 43.44% C; 2.26% H; 4.56% N.

 $[Pd(C_6F_5)I(SPPy_2Ph)]$ (2c). To $[Pd(C_6F_5)Br(SPPy_2Ph)]$ (0.150 g, 0.220 mmol) in acetone (50 mL) was added KI (0.0415 g, 0.25 mmol). The mixture was stirred for 1 h. The acetone solution was evaporated to dryness, and the residue was extracted with dichloromethane (2 \times 15 mL). The potassium salts were insoluble. Addition of ethanol (15 mL) and evaporation of the solution to ca. 10 mL afforded an orange compound, which was filtered, washed with ethanol, and airdried. Yield: 0.194 g, 84%. Calcd: 38.82% C; 1.92% H; 4.11% N. Found: 38.79% C, 1.85% H; 4.01% N.

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Supplementary Material Available: Listing of atomic coordinates, full tables of bond distances and bond angles, and a listing of anisotropic displacement parameters (4 pages). Ordering information is given on any current masthead page.

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