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[5] Based on the assumption that the complexation at the ammonium ion moieties of **7** are independent of each other the association constant for pseudorotaxane formation between the ammonium ion moieties of **7** and DB24C8 in [D$_6$]acetone/[D$_3$]chloroform (1/1) at 22 °C was calculated as $3.5\times10^{2}\,\text{M}^{-1}$ by single point measurement (slow exchange) by using ^{1}H NMR spectroscopy.

[6] The NOESY spectra of 1:1 stoichiometric solutions of **3a** and **7** could not be recorded at concentrations greater than 1.0 M because of overloading of the analogue to digital converter.

[7] The average molecular weight of **9** was calculated on the assumption that the cyclic oligomers such as 2:2 and 3:3 complexes were absent. It is noteworthy that linear polymerization is highly favored over cyclization at high solution concentrations (for example, 1.0 M). For reviews on cyclization versus linear polymerization, see a) G. Odian, *Principles of Polymerization*, 3rd ed., Wiley, New York, **1991**, p. 73; b) S. C. Hamilton, J. A. Semlyen, *Polymer* **1997**, *38*, 1685–1691. Therefore, the assumption of the absence of the oligomeric cyclic complexes is valid in the more concentrated solutions. The percentage of ammonium ion units l in **9** is equal to 100 minus the percentage of ammonium ion units d in **8** ($l+d=100$) The ratio of the percentage of ammonium ion units l in **9** to the percentage of uncomplexed ammonium ion units u is equal to $2n$ (n = degree of aggregation). Thus, this equation yields $n=(100\,\% - d/2u)$. From the n value and the repeat unit mass (1980 Da) the number average molar mass M_n of **9** was calculated.

[8] A mixture of acetone/chloroform (1/1) was added to a flask containing **3a** (1.1233g) and **7** (0.8568 g) until complete dissolution occurred. The solution was slowly concentrated and vacuum dried to afford **9**, which was then diluted with acetone/chloroform (1/1) to 0.50 mL.

[9] Similar effects have been observed in a supramolecule assembled from a heteroditopic precursor. See N. Yamaguchi, D. S. Nagvekar, H. W. Gibson, *Angew. Chem.* **1998**, *110*, 2518–2520; *Angew. Chem. Int. Ed.* **1998**, *37*, 2361–2364.

[10] The ^{1}H NMR spectrum of a 1:1 stoichiometric solution of **1b** and dibenzylammonium hexafluorophosphate at 1.0×10^{-2} M in [D$_6$]acetone/[D$_3$]chloroform (1/1) did not show extra sets of signals from slow exchange or changes in the chemical shifts from fast exchange. The *m*-phenylene linkage prevents pseudorotaxane formation in solution.

[11] The solutions were frozen at −93 °C with an acetone–ethanol/liquid nitrogen bath and the solvents were removed under high vacuum to give yellow–orange solids.

[12] To eliminate sample history the freeze-dried samples were initially heated to 100 °C and cooled to 30 °C at the rate of 10 °C min^{-1}. They were then heated at 10 °C min^{-1} and the DSC thermograms were recorded.

[13] The ^{1}H NMR spectra of equimolar solutions of **3a** and **7** at 1.0×10^{-2}, 0.10, and 0.50 M in [D$_6$]acetone/[D$_3$]chloroform (1/1) were essentially unchanged from −40 to −60 °C. Below this temperature the ^{1}H NMR spectra of the solutions were unable to be recorded because of partial freezing of the solvents. Thus, M_n values of the freeze-dried (−93 °C) samples were estimated by simple integration of relevant signals of the spectra recorded at −40 °C.

[14] A similar dimeric cyclic species has recently been reported: P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1344–1347; *Angew. Chem. Int. Ed.* **1998**, *37*, 1294–1297.

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Cleavage of Palladium Metallacycles by Acids: A Probe for the Study of the Cyclometalation Reaction**

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The cyclometalation reaction[1] constitutes one of the first known examples of $C-H$ bond activation, which is a major achievement of organometallic chemistry.[2] Of particular interest is the cyclometalation of a pendant aromatic ring, a process that constitutes a good model for $C-H$ activation and has in addition led to many useful synthetic applications.[3–6]

Despite the number of studies devoted to this transformation,[7] contemporary work continues to provide important mechanistic information.[1a] A recent account by Canty and van Koten has pointed out the formal relationship that may be established between the cyclometalation reaction and the protonation of $M-CH_3$ and $M-C_6H_5$ bonds,[8] as well as the possible intermediary role of arenonium ions in both processes.[8, 9] Here we provide experimental evidence in support

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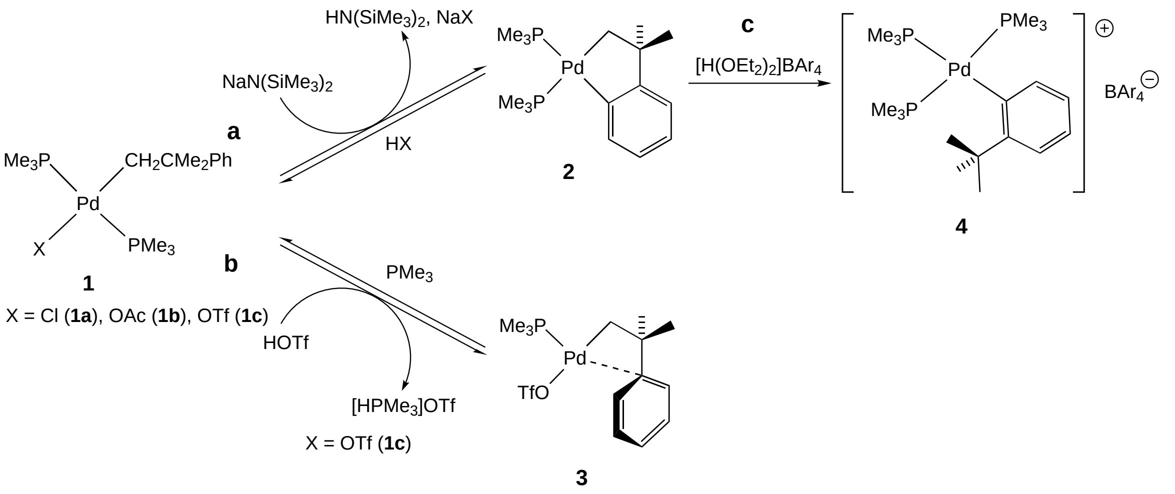
[**] Financial support from the Dirección General de Investigación Científica y Técnica (Project PB96-0824) and Junta de Andalucía is gratefully acknowledged. J.A.L thanks the CONACYT and the University of Guanajuato (Mexico) for a studentship. E.S. was an Erasmus student in our laboratory from the University of Hamburg. We thank Professors M. Brookhart and R. A. Andersen for helpful discussions during their sabbatical stays in our laboratory as Iberdrola Visiting Professors. Thanks are also given to Iberdrola for making their stay possible.



Scheme 1.

of this proposal by: 1) the synthesis of the palladacycle **2** (Scheme 1) by the base-induced metalation of the neophyl derivatives *trans*-[Pd(CH$_2$CMe$_2$Ph)X(PMe$_3$)$_2$] (X = Cl, **1a**; OAc, **1b**; OTf, **1c**) and 2) the study of the reverse reaction, namely the protonation of **2** to produce compounds of types **1** and **3** or the aryl derivative [Pd(C$_6$H$_4$-*o*-CMe$_3$)(PMe$_3$)$_3$]BAr$_4$ (**4**, Ar = 3,5-C$_6$H$_3$(CF$_3$)$_2$, Scheme 1). As discussed below one of the intermediates in our system is a cationic species **B** (Scheme 2), in which the highly electrophilic palladium center is stabilized by an auxiliary π,η^1 interaction with the *ipso* carbon atom of the phenyl group.[10]

In contrast with the behavior exhibited by the analogous Ni^{II} and Pt^{II} neophyl derivatives, which convert readily into the corresponding metallacycles,[7c, 11a] the bis(alkyl) complex [Pd(CH$_2$CMe$_2$Ph)$_2$(PMe$_3$)$_2$] fails to give a product of this kind,[11b] even though related palladacyclic species can be easily prepared.[12] Nonetheless, metallacycle **2** can be formed by treatment of the neophyl complexes **1** with a strong base such as NaN(SiMe$_3$)$_2$ (Scheme 1, reaction a). This method parallels the previously reported synthesis of other related palladium metallacycles.[12] The cyclometalation reaction can be readily reversed by treating **2** with stoichiometric amounts of HX (X = Cl, OAc, HTfO) to give **1**. This regioselectivity is the same as that found in the analogous Ni metallacycle.[11a] The triflate complex **1c** is very labile and, whereas it has been fully characterized in solution, it could not be isolated in pure, crystalline form. If two equivalents of triflic acid (HOTf) are used, high yields of the crystalline complex **3** are obtained along with [HPMe$_3$]OTf (Scheme 1, reaction b). This latter transformation can also be reversed; the addition of PMe$_3$ to solutions of **3** regenerates the neophyl compound **1c**.

The structure proposed for **3** on spectroscopic grounds has been confirmed by X-ray studies. Figure 1 shows an ORTEP view of one of the two crystallographically independent molecules of **3** that are contained in the unit cell.[13] The most interesting aspect of this highly distorted square-planar structure is undoubtedly the coordination mode of the neophyl ligand. The Pd–CH$_2$ bond has a normal length (ca. 2.02 Å) but the neophyl backbone bends in such a way that the phenyl ring comes close to the Pd atom (Figure 1, Table 1). Thus, the relatively short Pd–C$_{ipso}$ distance of about 2.38 Å is indicative of a π-bonding interaction. Since the *ortho* carbon atoms are farther apart (the shortest Pd–C$_{ortho}$ distances being 2.61(2) and 2.53(1) Å in the two independent molecules, respectively), the coordination of the ring can be described as approximately π,η^1. This is in accord with a similar observation by Falvello, Forniés, and co-workers in the complex *cis*-[Pd(C$_6$F$_5$)$_2$(NMe$_2$CH$_2$C$_6$H$_5$)],[10a] although for other related Pd–arene complexes π,η^2 coordination of the arene ligand has been proposed.[10c,d]

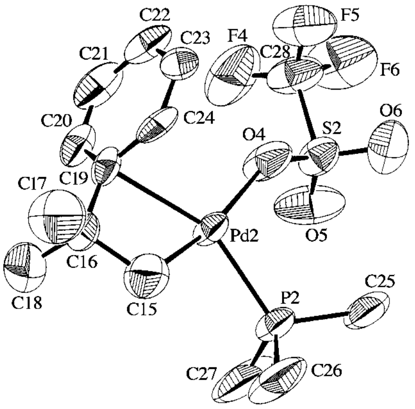


Figure 1. ORTEP representation of one of the two crystallographically independent molecules of **3**.

Table 1. Selected bond lengths [Å] and angles [°] for **3**.

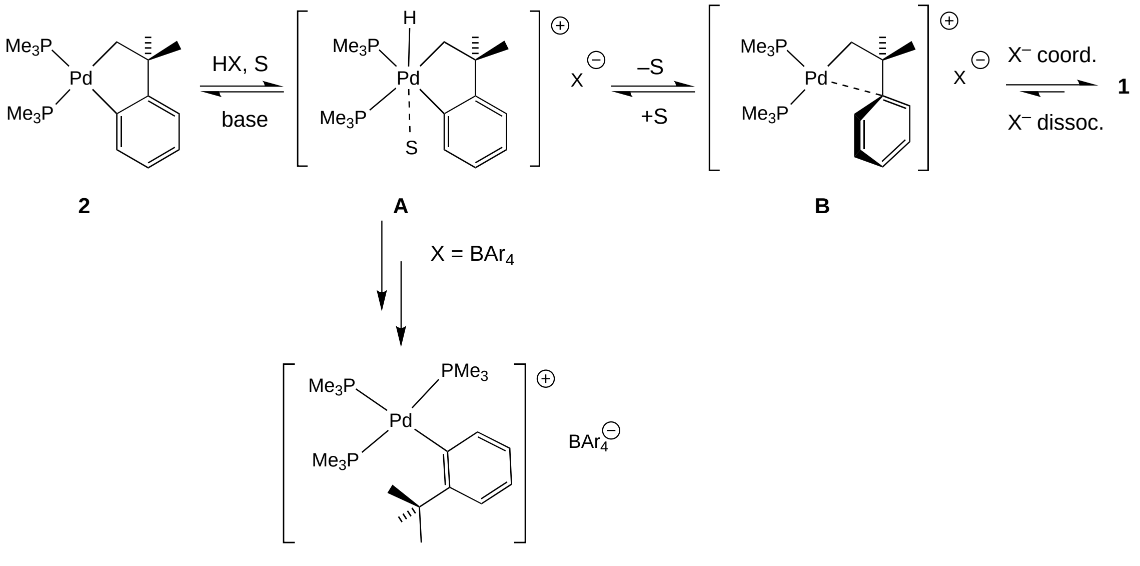
Molecule A		Molecule B	
Pd1–P1	2.233(4)	Pd2–P2	2.232(4)
Pd1–O1	2.21(1)	Pd2–O4	2.16(1)
Pd1–C1	2.02(2)	Pd2–C15	2.01(2)
Pd1–C5	2.38(1)	Pd2–C19	2.39(1)
P1-Pd1-O1	99.7(3)	P2-Pd2-O4	99.9(3)
P1-Pd1-C1	90.2(5)	P2-Pd2-C15	90.9(5)
P1-Pd1-C5	153.8(4)	P2-Pd2-C19	154.0(4)
O1-Pd1-C1	170.0(5)	O4-Pd2-C15	169.2(6)
O1-Pd1-C5	104.6(4)	O4-Pd2-C19	104.6(5)
C1-Pd1-C5	65.4(6)	C15-Pd2-C19	64.9(6)

1433-7851/99/3801-0148 $ 17.50+.50/0

The formation of **3** is particularly noteworthy because π–arene complexes have been proposed to be intermediates in the activation of aromatic C–H bonds by Pd and other metals.[14] The recent observation by Cheng and co-workers of the cyclometalation of a neutral palladium π–arene complex by treatment with sodium hydroxide in the presence of PPh_3,[1m] seems to indicate the intermediacy of this type of complex in the cyclometalation reaction. Unfortunately, direct cyclometalation of **3** by bases under the experimental conditions used by Cheng et al. has proved meaningless, because the π–arene interaction is readily cleaved by added PMe_3.[15] Nevertheless, **3** is a robust compound that can be dissolved in CD_3OD without decomposition.[16] No H–D exchange, in the *ortho* positions of the phenyl ring could be detected after three days at room temperature (or 6 h at 60 °C) in this solvent, which suggests these protons are not labile.

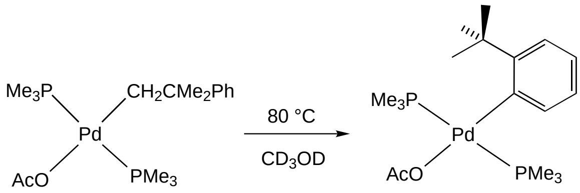
At variance with the protonations described above, the reaction of the metallacycle **2** with one equivalent of $[H(OEt_2)_2]BAr_4$[17] (Ar = 3,5-$C_6H_3(CF_3)_2$) in Et_2O (–40 °C, then warmed to room temperature) leads to the aryl derivative **4**, in 42 % yield (Scheme 1, reaction c), together with some as yet unidentified products. The nature of **4** would appear to suggest a different regioselectivity for the protonation reaction, namely proton attack at the sp^3 alkyl carbon atom. However, carrying out the reaction in CH_2Cl_2 at –40 °C or, alternatively, treating the $[Pd(CH_2CMe_2Ph)X(PMe_3)_2]$ complexes **1a** or **1c** with $NaBAr_4$, also in CH_2Cl_2 at low temperature, allows the isolation of a colorless complex **B** (Scheme 2, X = BAr_4). This complex has spectroscopic properties related to those of **3**, which is indicative of a π,η^1–arene coordination ($^{31}P\{^1H\}$ NMR: AX spin system, $\delta_A = -1.8$, $\delta_X = -31.1$, $^2J_{AX} = 37$ Hz; $^{13}C\{^1H\}$ NMR: $\delta = 33.5$ (dd, $^2J_{CP} = 65$, 8 Hz, Pd-CH_2), 123.5 (dd, $^2J_{CP} = 12$, 4 Hz, C_{ipso})). Dissolution of **B** in Et_2O or THF results in formation of the above-mentioned mixture of **4** plus unidentified products. On the basis of these data we propose that the protonation occurs also at the aryl carbon atom to give initially compound **B** (that is, the kinetic product, see below) and that **B** subsequently isomerizes by a solvent-assisted rearrangement of the neophyl ligand (Scheme 2). We are not aware of a similar role of the solvent in related isomerizations of M–$CH_2CMe_2C_6H_5$ moieties.[11e, 18–20]

We have been unable to obtain experimental evidence for the formation of intermediate **A** (Scheme 2), hence its participation in the proposed reaction pathway remains speculative. However it appears reasonable on chemical grounds and moreover its formulation is in agreement with recent results on organopalladium(IV) and hydridoplatinum(IV) chemistry.[8, 9, 21] As a consequence of the higher kinetic barrier to the reorientation of the strongly directional sp^3 orbital of the alkyl $PdCH_2$ carbon atom relative to the sp^2 aryl carbon atom, to form the C–H bond,[22] hydrogen transfer to the aryl carbon atom is expected to be kinetically more favorable. This would yield the cationic species **B**, perhaps with participation of an arenonium ion or an agostic intermediate (not ilustrated in Scheme 2).[9, 21] Coordination of X^- would convert **B** into compounds **1** but if X^- is a noncoordinating anion, for example BAr_4^-, **B** could reverse to the purported Pd^{IV} hydride **A** in a process that seems to require the presence of Et_2O or THF as a weakly coordinating solvent. Eventually, complex **A** could undergo the kinetically less-favorable 1,2 hydrogen shift to the sp^3-hybridised alkyl site, followed by phosphane substitution to give compound **4**. There are still some aspects of these transformations that are only partially understood and the overall process of Scheme 2 may be mechanistically more complex than depicted. However in agreement with the above hypothesis, treatment of **2** with $[HPMe_3]BAr_4$ in CH_2Cl_2 gives $[Pd(CH_2CMe_2Ph)(PMe_3)_3]BAr_4$, which converts cleanly into **4** after heating at 60 °C for three hours. A similar isomerization of the neophyl ligand occurs when **1b** is heated at 80 °C in CD_3OD for three



Scheme 2.

hours, with the aryl compound *trans*-[Pd(C_6H_4-*o*-CMe_3)(OAc)(PMe_3)$_2$] (**5**) being formed in good yield. Only 10% isomerization is observed after three hours in C_6D_6 under the same reaction conditions.



1b **5**

In closing, some comments on the chemical significance of the cationic species **B** seem appropriate. As noted above, **B** is involved as an intermediate in both the cyclometalation and the isomerization of the neophyl ligand although the additional participation in the key C–H bond activation reaction of an arenonium ion or an agostic intermediate appears likely. The lability of **B** contrasts with the relative inertness of the neutral triflate complex **3**. This observation suggests that a positive charge at the Pd center may be needed to achieve the metalation of the pendant aromatic ring. In other words, anion dissociation rather than phosphane dissociation could be required for the activation of the C–H bond in compounds of type **1**. This proposal is in agreement with previous findings on somewhat related reactions.[23] Moreover, it is in accord with our failure to cyclometalate the bis(alkyl) complex [Pd(CH_2CMe_2Ph)$_2$(PMe_3)$_2$].[11e]

Experimental Section

2 and **3**: The metallacyclic precursor **2** was prepared by treating a solution of complex **1a** (0.21 g, 0.5 mmol) in THF (30 mL) at $-50\,^{\circ}C$ with $NaN(SiMe_3)_2$ (0.85 mL, 0.6 M solution in toluene, 0.5 mmol) and was isolated as white crystals (ca. 40% yield) from its solutions in diethyl ether or diethyl ether/petroleum ether mixtures. Elemental analysis calcd for $C_{16}H_{30}P_2Pd$: C 49.18, H 7.68; found: C 49.22, H 7.56; ^1H NMR (CD_2Cl_2, 20 °C): $\delta = 2.20$ (dd, 2H, $^3J_{HP} = 8.8$, 5.7 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) AX spin system, $\delta_A = -22.9$, $\delta_X = -27.9$, $J_{AX} = 23$ Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): $\delta = 52.5$ (dd, $^2J_{CP} = 95$, 9 Hz, CH_2), 169.2 (dd, $^2J_{CP} = 123$, 14 Hz, C_q arom.). A solution of HOTf in Et_2O (3.8 mL, 0.53 M, 2 mmol) was added dropwise to a cold solution ($-80\,^{\circ}C$) of a pure, crystalline sample of this compound (0.39 g, 1 mmol) in Et_2O (40 mL). The mixture was stirred for 2.5 h at room temperature, the solvent evaporated under vacuum, and the residue extracted with Et_2O. The white precipitate of $HPMe_3^+TfO^-$ was separated by filtration, and the solution concentrated and cooled overnight at $-20\,^{\circ}C$. The product was isolated as colorless crystals (290 mg, 75%). Elemental analysis calcd for $C_{14}H_{22}F_3O_3PSPd$: C 36.18, H 4.77; found: C 36.34, H 4.60; ^1H NMR (CD_2Cl_2, 20 °C): $\delta = 1.46$ (d, 2H, $^3J_{HP} = 5.6$ Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): $\delta = -2.85$ s; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): $\delta = 24.3$ (d, $^2J_{CP} = 4$ Hz, CH_2), 121.8 (d, $^2J_{CP} = 13$ Hz, C_q arom.), 123.2 (s, 2CH arom.), 131.2 (s, 1CH arom.), 132.3 (s, 2CH arom.).

4: A solution of compound **2** (0.1 g, ca. 0.25 mmol) in Et_2O (40 mL) was cooled at $-40\,^{\circ}C$, and treated with $[H(OEt_2)_2]BAr_4$ (0.25 g, 0.25 mmol) dissolved in Et_2O (10 mL). The mixture was stirred for 1 h at room temperature. The solvent was then removed in vacuo, and the residue extracted with Et_2O (30 mL). The volume was reduced to approximately one half and petroleum ether added until the solution became slightly cloudy. After cooling the mixture at $-20\,^{\circ}C$ overnight, the product was collected as colorless crystals, which were filtered, washed with petroleum ether, and dried (140 mg, 42%). Elemental analysis calcd for $C_{51}H_{52}BF_{24}P_3Pd$: C 46.02, H 3.94; found: C 46.37, H 3.88; ^1H NMR (CD_2Cl_2, 20 °C): $\delta = 1.44$ (s, 9H, CMe_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) AX_2 spin system, $\delta_A = -27.6$, $\delta_X = -17.2$, $J_{AX} = 44$ Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): $\delta = 33.0$ (s, CMe_3), 36.9 (s, CMe_3), 151.7 (d, $^2J_{CP} = 107$ Hz, C_q arom.).

Received: May 5,
Revised version: July 31, 1998 [Z11819IE]
German version: *Angew. Chem.* **1999**, *111*, 199–203

Keywords: C-H activation · metallacycles · palladium · pi interactions · protonations

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[13] Crystallographic data for **3**: a yellow irregular crystal of $PdC_{14}H_{22}F_3O_3PS$ having approximate dimensions of 0.26 × 0.15 × 0.34 mm was mounted in a glass capillary under argon. All measurements were performed on a Rigaku AFC6S diffractometer with

graphite monochromated $Mo_{K\alpha}$ radiation; $M_r = 464.76$; triclinic, space group $P1$ (no. 2), $a = 11.428(3)$, $b = 17.336(4)$, $c = 10.439(5)$ Å, $\alpha = 98.11(3)$, $\beta = 104.13(3)$, $\gamma = 106.02(2)^\circ$, $V = 1879(2)$ Å^3, $\rho_{calcd} = 1.643$ g cm^{-3}, $F(000) = 936$, $T = 293$ K, ($\lambda = 0.71069$ Å), $\mu(Mo_{K\alpha}) = 12.0$ cm^{-1}, scan = $\omega/2\Theta$, scan rate = 8.0° min (in ω; 3 scans), scan width $(1.10 + 0.30\tan\Theta)^\circ$, $2\Theta_{max} = 50.1^\circ$. Of the 5734 reflections measured through a detector aperture 6.0 mm horizontal and 6.0 mm vertical, 5455 were unique ($R_{int} = 0.120$). A decay correction was applied following the intensities of three standard reflections measured after every 100 reflections (-6.80% during data collection). The absorption correction was neglegible and it was not applied. The data were corrected for Lorentz and polarization effects. A structural solution was found by direct methods (Patterson method, MITHRIL program).[24] The least-squares refinement was performed for a total of 415 parameters with 2976 reflections ($I > 3\sigma(I)$); minimization function: $\Sigma w(|F_o| - |F_c|)^2$, with least-squares weights: $4F_o^2/\sigma^2(F_o^2)$, p factor = 0.03. The non-hydrogen atoms were anisotropically refined and the hydrogen atoms were included at idealized positions and they were not refined. $R_F = 0.060$, $R_w = 0.070$, GOF = 2.03, maximum shift/error: 7.26. Accurate cell dimensions were obtained by least-squares refinement of 25 reflections ranged $13.40 < 2\Theta < 16.44^\circ$. All calculations were performed on a VAX 3520 station at the Servicio Central de Ciencias y Tecnologia de la Universidad de Cádiz. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101361 . Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[15] Compound **3** reacts rapidly with one equivalent of PMe_3 to give **1b**.

[16] The $^{13}C\{^1H\}$ NMR spectra of **3** in CD_2Cl_2 and CD_3OD are very similar. Since the signal assigned to the Pd-bonded aromatic quaternary carbon atom appears in both cases as a doublet ($^2J_{CP} = 7$ Hz) the π,η^1 arene interaction seems to be maintained in methanol.

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Spin-Orbit Coupling versus the VSEPR Method: On the Possibility of a Nonplanar Structure for the Super-Heavy Noble Gas Tetrafluoride $(118)F_4$**

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The discovery of the super-heavy elements 110, 111, and 112 by Armbruster and co-workers during the 1990s[1] has stimulated new interest in the properties and chemistry of newly discovered elements.[2, 3] Elements 110, 111, and 112 complete the 6d block of the periodic table. The next elements likely to be discovered are the representative 7p block elements, those with atomic numbers 113–118. The last of these, element 118, is predicted to be a noble gas with a closed-shell $7s^26d^{10}7p^6$ electron configuration. As such, its properties are expected to resemble those of the heavy noble gases Xe and Rn, which are known to form compounds with electronegative elements such as F.[4]

The correct prediction of the structures of noble gas compounds was one of the great successes of the valence-shell electron-pair repulsion (VSEPR) model of Gillespie and Nyholm, in both its original[5] and more-refined current[6] formulations. This simple and pedagogically useful model correctly predicted that NgF_2 and NgF_4 (Ng = noble gas) should adopt linear and square-planar molecular geometries, respectively, based on trigonal-bipyramidal and octahedral electron-pair geometries. Herein, we will focus on the noble gas tetrafluorides XeF_4, which is known,[7] RnF_4, which has not been characterized definitively,[8] and $(118)F_4$. Our interest in the bonding in compounds of the super-heavy elements stems in part from the huge spin-orbit effects exhibited by these elements by virtue of their large atomic numbers.[9] These relativistic effects can have a remarkable influence on the properties of atoms and compounds of these elements. For example, Kaldor et al. have used relativistic coupled cluster calculations to predict that relativistic stabilization of the 8s orbital causes the element 118 to have a small electron affinity, making it unique among the noble gases.[10] We have recently predicted that spin-orbit effects will cause the super-heavy hydrogen halide H(117) to have an unusually long and strong bond.[11] Here we will report that the influence of spin-orbit effects on the bonding in $(118)F_4$ is so great as to favor a non-VSEPR tetrahedral structure for this molecule.

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[**] This work was supported by the Division of Chemical Sciences, US Department of Energy (Grant DE-FG02-86ER13529), by the Ohio Supercomputer Center, and by the National Energy Research Supercomputer Center. We are grateful to W. C. Ermler, D. C. Hoffman, R. M. Pitzer, and P. Schwerdtfeger for helpful comments.