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Synthesis, structure and computational studies of a cationic T-shaped Pd-complex†

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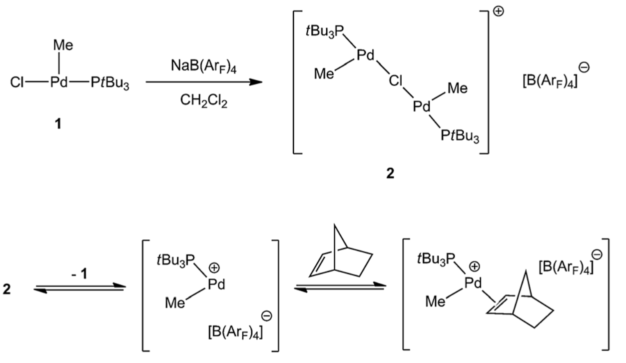
Reaction of [(cod)Pd(Me)(thf)][SbF_6] or [(cod)Pd(Me)(MeCN)][$B(Ar_F)_4$] (cod = 1,5-cyclooctadiene, $B(Ar_F)_4$ = [3,5-$(F_3C)_2C_6H_3]_4B$) with one or two equivalents of $t$$Bu_3P$ gives [$(tBu_3P)_2Pd(Me)]^+$ (**3**) exclusively. The two sterically encumbered tBu-groups prevent solvent coordination. In addition, this formally three coordinate complex is stabilized by a γ-agostic interaction in solid state, whereas solution NMR studies confirm that this interaction is rather weak. The strength of the γ-agostic interaction was evaluated using density functional theory (DFT) calculations. Surprisingly, [$(tBu_3P)_2Pd(Me)]^+$ is unreactive toward CO, H_2, C_2H_4 and norbornene.

Introduction

Vacant coordination sites on transition metal complexes are a prerequisite for many classic organometallic reactions.[1] Consequently, unsaturated metal complexes are proposed intermediates in catalytic cycles such as hydrogenation, polymerization, cross-coupling reactions and C–H bond activation and functionalization.[1,2] An interesting sub-class in this context are 3-coordinate, T-shaped d^8-transition metal complexes which are relevant in cross-coupling reactions or in the stabilization of unusual molecules.[3–12] Consequently such species have been probed by many computational investigations.[13–16] However, truly T-shaped, 3-coordinate complexes have remained elusive with the exception of Pt–boryl complexes such as *trans*-[$(Cy_3P)_2Pt\{B(Fc)Br\}$][$B(Ar_F)_4$] ($B(Ar_F)_4$ = [3,5-$(F_3C)_2C_6H_3]_4B$);[17,18] in fact most of the formally 3-coordinate complexes are stabilized by (weak) agostic interactions.[3–6,9–12,16,19–22]

In the course of our investigations on the vinyl addition polymerization of norbornene (NB)[23–25] we began to investigate whether one could synthesize a cationic species of the type [$(tBu_3P)Pd(Me)(solvent)]^+$ (**A**) which would provide a cationic Pd complex with a very open coordination sphere while overcoming the limitations of the originally introduced [($t$$Bu_3P$)PdCl(Me)] (**1**)/Ag[$B(Ar_F)_4$] system which forms the dimer [$(tBu_3P)_2Pd_2(Me)_2Cl$][$B(Ar_F)_4$] (**2**) upon chloride abstraction (Scheme 1). The dimer acts as a precatalyst but requires the dissociation into [($t$$Bu_3P$)PdCl(Me)] and [$(tBu_3P)Pd(Me)]^+$ (the active species) prior to polymerization.[20] While this catalyst system can polymerize certain functionalized norbornenes in a living manner with moderate activity, the polymerization of the more reactive unfunctionalized NB is non-living as judged from the polymerization data.[20] Catalyst architecture **A** would overcome this dissociation problem. The cationic nature of **A** would likely lead to a stabilizing intramolecular γ-agostic interaction between the tBu groups and the cationic Pd center. In this contribution we report on our attempts to synthesize **A**, the synthesis of [$(tBu_3P)_2Pd(Me)]^+$ (**3**), which is a rare example of a formally 3-coordinate cationic Pd complex, and some reactivity and computational studies concerning **3**.



Scheme 1

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Results and discussion

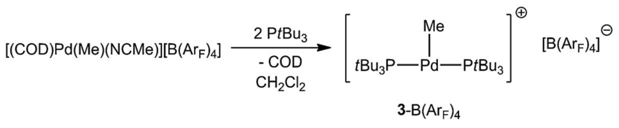
Synthesis

Complex **1** was synthesized, and NMR experiments in CD_2Cl_2 showed that on addition of $AgSbF_6$ or $NaB(Ar_F)_4$ only the dimer **2** was formed. On addition of 20 equivalents of NB polymerization occurs, while most of **2** remains unreacted. This suggests that the dissociation of **2** is responsible for the slow initiation (relative to propagation) of this catalyst system and only for the less reactive functionalized NB derivatives does the rate of polymerization become competitive to the rate of initiation. From this study it was concluded that $[(tBu_3P)Pd(Me)(solvent)]^+$ (**A**) would overcome this limitation. We therefore attempted to perform the chloride abstraction in coordinating solvents such as diethyl ether to stabilize the cationic intermediate as a mono solvent adduct, $[(tBu_3P)Pd(Me)(OEt_2)]^+$. However, these attempts were unsuccessful.

Consequently, an alternative starting material was investigated in which the chloride group has already been removed and therefore should overcome the formation of the chloride dimer, **2**. In this context, $[(cod)Pd(Me)(MeCN)][B(Ar_F)_4]$ (cod = 1,5-cyclooctadiene), which is readily prepared *in situ* from $[(cod)Pd(Me)(Cl)]$ on addition of $Na[B(Ar_F)_4]$ in a mixture of CH_2Cl_2 and MeCN was chosen.[26] However, on addition of tBu_3P only the bis(phosphine) adduct **3**-$B(Ar_F)_4$ was isolated regardless of the reaction conditions and the stoichiometry (Scheme 2). Complex **3**-$B(Ar_F)_4$ was obtained as green crystals that are air stable. The ^1H NMR spectrum of **3**-$B(Ar_F)_4$ shows, in addition to the $B(Ar_F)_4$ counteranion signals, only resonances due to tBu_3P and Me in the correct ratio of 36 : 3. No additional solvent coordination to the cationic Pd center is observed. In addition, **3**-$B(Ar_F)_4$ exhibits a single $^{31}P\{^1H\}$ NMR resonance (δ 64.4) and two ^1H NMR resonances for the Me and CMe_3 groups at δ 2.12 (t, $^3J_{PH}$ = 4.4 Hz) and δ 1.54 (J_{PH} = 6.4 Hz), respectively. This suggests equivalent P and *t*Bu groups on the NMR time scale at ambient temperature; no decoalescence was observed on cooling of the sample to −80 °C. The low solubility of this molecule prevented variable temperature (VT) NMR studies at even lower temperatures. The solution behavior is consistent with a 3-coordinate Pd(II) complex which might be stabilized by an additional weak agostic interaction. The related cationic $[Pt(Me)(iPr_3P)_2]^+$ complex behaves similarly, but undergoes acid-catalyzed intramolecular CH-activation.[12]

Solid state structure

To evaluate the presence of agostic interactions we attempted to obtain a molecular structure using single crystal X-ray diffraction data. Unfortunately, crystals of **3**-$B(Ar_F)_4$ were not suitable for X-ray diffraction, so we decided to exchange the anion $[B(Ar_F)_4]^-$ for $[SbF_6]^-$. The starting material of choice was $[(cod)Pd(Me)(thf)][SbF_6]$, which is readily prepared from $[(cod)Pd(Me)(Cl)]$ on addition of $AgSbF_6$ in tetrahydrofuran.[27] Addition of tBu_3P in tetrahydrofuran yielded **3**-SbF_6 and single crystals were grown from a saturated CH_2Cl_2 solution at −25 °C.‡ Fig. 1 shows an ORTEP representation of the molecular structure of **3**-SbF_6, and selected bond distances and angles are given in the caption. At first glance this molecule may be regarded as a 3-coordinate, T-shaped cationic $[(tBu_3P)_2Pd(Me)]^+$ complex. However, a closer inspection of the structure reveals an interaction (2.900(7) Å) between the cationic Pd atom and C11 on P1. This value is within the usual range for agostic interactions observed for Pd.[5,20]



Scheme 2

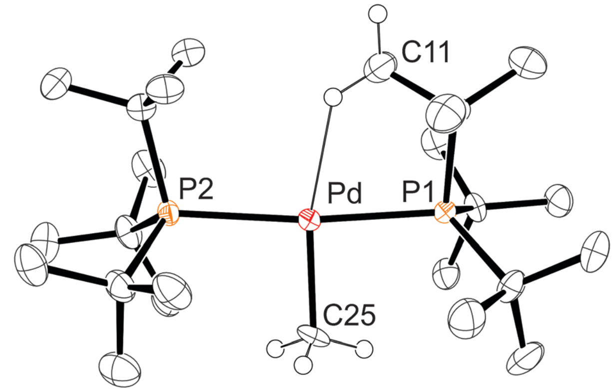


Fig. 1 ORTEP diagram for **3**-SbF_6 (ellipsoids drawn at the 50% probability level). The $[SbF_6]^-$ counter anion and most H-atoms were omitted for clarity. Selected bond distances (Å) and angles (°): Pd–P1 2.3483(15), Pd–P2 2.4353(15), Pd–C25 2.029(6), Pd–C11 2.900(2), P1–Pd–P2 173.40(5), P1–Pd–C25 91.4(2), P2–Pd–C25 95.1(2).

Therefore, the cationic complex **3** exhibits a similar stabilizing γ-agostic interaction to that of neutral precursor **1** to give a 4-coordinate square-planar Pd center. The solution behavior indicated that this γ-agostic interaction is rather weak and thus the reaction chemistry of **3** might provide additional insight into the strength of this interaction. Surprisingly, **3** is unreactive toward H_2, C_2H_4, and norbornene, and no adduct formation was observed with the sterically undemanding ligand, CO (even at low temperature). In addition, no significant change in the chemical shifts of **3** is observed on addition of a good σ-donor such as MeCN thus ruling out any coordination. We also attempted to protonate **3** with $[H(OEt_2)_2][B(Ar_F)_4]$, but no reaction occurs similar to the previous results on $[(PONOP)PdMe][B(Ar_F)_4]$ (PONOP = 2,6-$(tBu_2PO)_2C_5H_3N$).[28] Furthermore, no intramolecular CH-bond activation was observed as was seen in the case of $[Pt(Me)(iPr_3P)_2]^+$.[12]

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‡ Crystal data for **3**-SbF_6: $C_{25}H_{57}F_6P_2PdSb$, M_w = 761.80, monoclinic, a = 14.5334(6) Å, b = 14.2796(5) Å, c = 15.2101(5) Å, α = 90.00°, β = 92.956(3)°, γ = 90.00°, V = 3152.4(2) Å^3, T = 100(2) K, space group $P2/a$, Z = 4, MoKα, 9649 reflections measured, 6987 independent reflections. The final R_1 value was 0.0564 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1785 ($I > 2\sigma(I)$). The final R_1 value was 0.0807 (all data). The final $wR(F^2)$ value was 0.1953 (all data). The goodness of fit on F^2 was 1.079.

Computational studies

In view of this unexpected (and disappointing) reaction chemistry of **3**, we decided to quantify the strength of the γ-agostic interactions in complexes **1**, **3**, **4** and **5** (Fig. 2). These Pd-complexes can be grouped into neutral (**1**), mono-cationic (**3**) and di-cationic (**4** and **5**) species. So the strength of the γ-agostic interaction can be evaluated as a function of complex charge. In addition, the calculations on **5** provide structural insights into a hypothetical σ-methane complex and these results were compared to $[(PONOP)Pd(CH_4)]^{2+}$ (**6**).

Previous DFT studies have shown that for alkane complexes weak non-covalent (dispersion) interactions need to be considered.[29] Hence, we decided to use the dispersion-corrected B97 functional, B97D (see Experimental section for details).[30] For comparison, we have also performed these calculations with the PBE0 functional which we have used previously for Rh and Ir pincer complexes.[28] The computed molecular geometries at the B97D level of theory are shown in Fig. 2 and a comparison between calculated and experimental structures for **1** and **3** is given in Table 1. Overall, the B97D results are in much better agreement with the experimentally determined structures. Therefore, we will focus our discussions only on the B97D results, but the PBE0 data are given in the ESI.† Although the computed and experimental structures agree reasonably well, the agostic interaction observed in solid state appears to be stronger (as judged by a shorter Pd···C distance) than in the calculated gas-phase structures. In addition, a small rotation barrier ($\Delta E^{\ddagger}$ = 9.5 kcal mol^{-1}) along the dihedral angle Pd–P1–C9–C11 (see ESI† for details) is computed

Table 1 Comparison between the calculated and experimental structures of complexes **1** and **3**

	1		**2**	
Complex	Exp.	Calc.	Exp.	Calc.
Pd–*P*	2.245(3)[a]	2.271[a]	2.348(2)[a] 2.435(2)[b]	2.387[a] 2.398[b]
Pd–CH_3	1.985(5)	2.059	2.029(6)	2.063
Pd–Cl	2.336(3)	2.332		
Pd···γ-*C*	2.84	3.212	2.90	3.320
Pd···γ-*H*		2.637		2.748

[a] P-atoms attached to the γ-agostic Me group. [b] P-atoms without γ-agostic Me interaction.

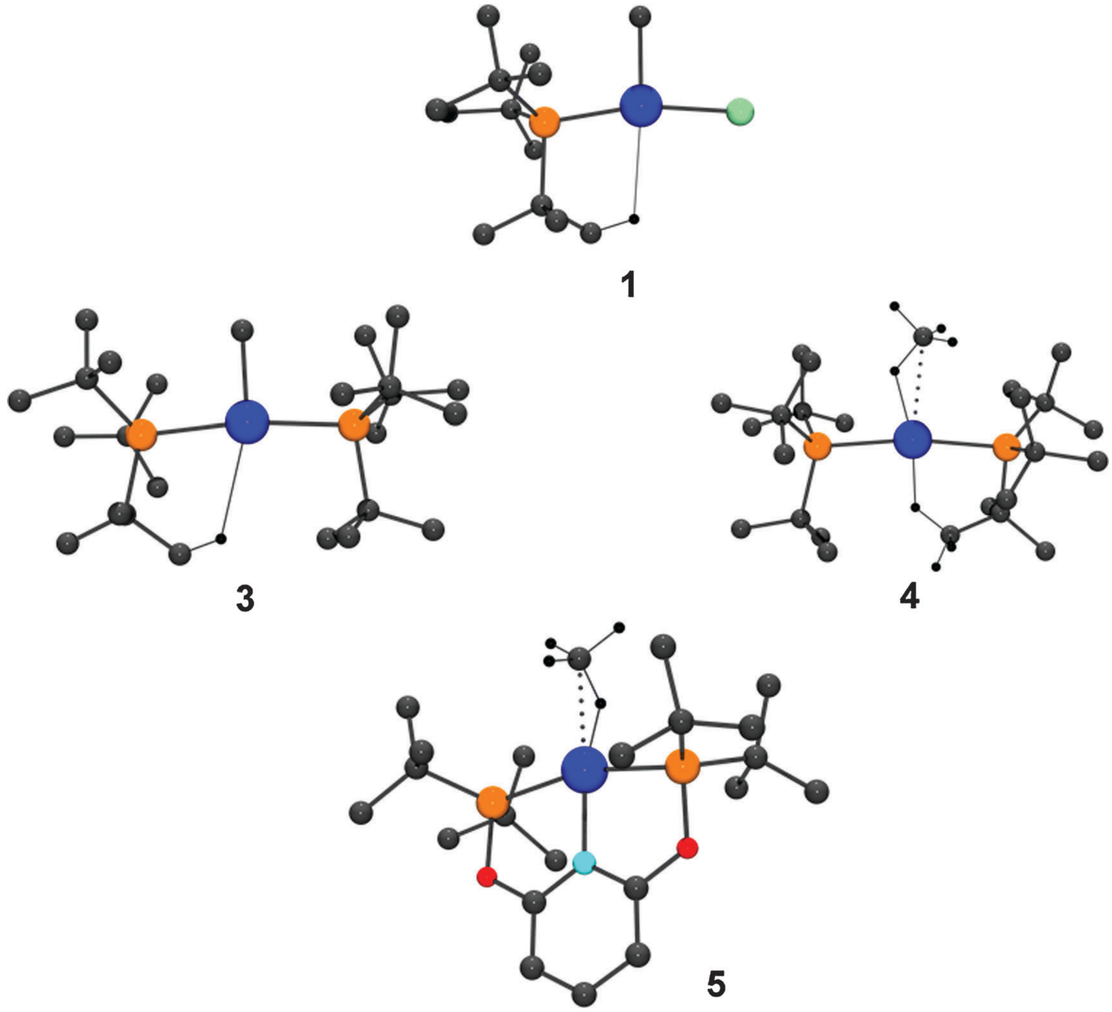

Fig. 2 Molecular geometries of **1**, **3**, **4**, **5** and **6** optimized at the B97D/6-311G(d,p) (C, H, N, O, P) and SDD (Pd) level.

which suggests only a weak γ-agostic interaction which is consistent with the solution VT NMR studies. Hence we attribute the differences between the computed and crystal structures to crystal packing effects.

For strong covalent bonds the bond dissociation enthalpy (BDE) and other indirect methods are frequently used to get an estimate for the intrinsic strengths of an individual bond,[31] but for the weaker agostic interactions this approach fails and only approximate values are proposed.[32] Hence, for agostic interactions the estimated values may range from 1 to 10 kcal mol^{-1}.[33–36] In addition, the separation between real values and artifacts can be exceedingly difficult. To overcome these limitations the concept of compliance constants is a useful tool to describe the mechanical strength of an individual bond or a non-covalent interaction,[37,38] which is, in principle, measurable by atomic force microscopy (AFM) of single molecules.[39] Furthermore, the generalized compliance matrix allows for a straightforward comparison of different molecular surroundings and has already been successfully applied to α-agostic interactions.[40] In an attempt to rationalize our experimental observations we extended this concept to γ-agostic and σ-methane interactions for which rather weak bonding interactions are expected. Unperturbed C–H bonds such as in CH_4 or P*t*Bu_3 have relaxed force constants in the range of 4.8–5.2 N cm^{-1}, and any strong agostic interaction should have a significant impact on this value. Table 2 lists the relaxed force constants for several Pd–X bonds or interactions. A closer inspection of the relaxed force constants for **1** and **3** also confirms that the interaction between the neutral or cationic Pd-atom and the γ-C or γ-CH bonds are weak. Hence, no significant perturbation of the relaxed force constants is observed. The situation gets more interesting for the hypothetical dicationic Pd-complexes **4** and **5**. In these molecules much stronger γ-agostic interactions are expected, and this is confirmed by computed compliance constants. The two dicationic σ-CH_4 complexes **5** and **6** show only weak methane binding and the calculated compliance constants for **6** predict a slightly stronger bond for this σ-CH_4 complex. Computations also show that CH_4 loss from the hypothetical dicationic Pd complex **4** proceeds essentially barrierless.

Table 2 Computed relaxed force constants (in N cm^{-1}) for complexes **1**, **3–6**

Complex	1	3	4	5	6
Pd–*P*	1.63^a	1.03^a	1.12^a	1.33/1.33^a	
		1.10^b	0.98^b		1.47^b
Pd–CH_3	1.76	1.72			
Pd···CH_4			0.19		0.26
Pd···CHH_3			0.53		0.35
Pd···γ-*C*	0.27	0.23	0.31	0.34/0.34	
Pd···γ-*H*	0.15	0.12	0.48	0.46/0.47	
C(CH_3)					
γ-*CH*···Pd	4.78	4.90	2.83	2.70/4.81	
CH_2 (ave.)	5.00	5.03	5.10	4.83/5.26	

[a] P-atoms attached to the γ-agostic Me group. [b] P-atoms without γ-agostic Me interaction.

Conclusions

Reaction of [(cod)Pd(Me)(thf)][SbF_6] (cod = 1,5-cyclooctadiene) with one or two equivalents of *t*Bu_3P gives [(*t*Bu_3P)$_2$Pd(Me)][SbF_6] exclusively. The sterically demanding *t*Bu-groups prevent additional solvent coordination and stabilize this formally three coordinate complex by a γ-agostic interaction in solid state, whereas solution studies confirm that this interaction is rather weak. Unfortunately, the sterically demanding *t*Bu-groups in combination with the γ-agostic interaction render [(*t*Bu_3P)$_2$Pd(Me)]$^+$ rather unreactive and consequently no reactivity with CO, H_2, C_2H_4 and norbornene was observed. The strength of this γ-agostic interaction was evaluated using relaxed force-constants and compared to a series of neutral and cationic Pd-complexes.

Experimental details

General considerations

All reactions, unless otherwise stated, were conducted under an atmosphere of dry, oxygen free argon using standard high-vacuum, Schlenk, or drybox techniques. Argon was purified by passing through a BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{13}C DEPT135 NMR spectra were recorded on a Bruker DRX 500 MHz, a Bruker DRX 400 MHz, or a Bruker 400 MHz AVANCE spectrometer. ^{1}H and ^{13}C chemical shifts are referenced relative to residual $CHCl_3$ (δ 7.24 for ^{1}H), CH(D)Cl_2 (δ 5.32 for ^{1}H), $CHCl_2F$ (δ 7.47 for ^{1}H), C_6HD_5 (δ 7.15 for ^{1}H), $^{13}CD_2Cl_2$ (δ 53.8 for ^{13}C), $^{13}CDCl_3$(δ 77.0 for ^{13}C), $^{13}CDCl_2F$ (δ 104.2 for ^{13}C) and $^{13}C_6D_6$ (δ 128.0 for ^{13}C); ^{31}P chemical shifts are referenced to an external standard of H_3PO_4. Probe temperatures were calibrated using methanol as previously described.[41] Elemental analyses were carried out by Robertson Microlit Laboratories of Madison, NJ.

Materials

All solvents were deoxygenated and dried by passage over columns of activated alumina.[42,43] CD_2Cl_2, purchased from Cambridge Laboratories, Inc., was dried over CaH_2, vacuum transferred to a Teflon sealable Schlenk flask containing 4 Å molecular sieves, and degassed *via* three freeze–pump–thaw cycles. [H(OEt_2)$_2$][B(Ar_F)$_4$],[44] Na[B(Ar_F)$_4$],[45] [(cod)Pd(Me)(Cl)],[46] and [(cod)Pd(Me)(thf)][SbF_6][27] were synthesized according to literature methods. All other reagents were purchased from Aldrich, Acros, Alpha Aesar or Strem Chemicals and used as received.

3-B(Ar_F)$_4$

Under an argon atmosphere a Schlenk tube was charged with [(cod)Pd(Me)(Cl)] (0.132 g, 0.5 mmol) and Na[B(Ar_F)$_4$] (0.44 g, 0.5 mmol). After cooling the flask to −40 °C CH_2Cl_2 (10 mL) and MeCN (10 mL) were added using a syringe. The reaction mixture was stirred while warming to −20 °C, resulting in the formation of [(cod)Pd(Me)(NCMe)][B(Ar_F)$_4$] accompanied by precipitation of NaCl. After allowing the precipitate to settle, the solution of the NCMe adduct was transferred *via* a cannula into another Schlenk flask cooled to 0 °C containing P*t*Bu$_3$ (0.202 g, 1 mmol) dissolved in a mixture of MeCN (4 mL) and CH$_2$Cl$_2$ (4 mL). The reaction mixture turned green immediately on addition and was stirred for 10 min. The solvent was removed under dynamic vacuum and the residue was dissolved in CH$_2$Cl$_2$ (*ca.* 5 mL) and a layer of pentane (10 mL) was added. Cooling to −20 °C and slow diffusion yielded green block like crystals (0.52 g, 0.37 mmol, 75%). ^{1}H NMR (CD$_2$Cl$_2$, RT): δ 7.30 (s, 8H, *o*-Ar, B(Ar$_F$)$_4$), 7.16 (s, 4H, *p*-Ar, B(Ar$_F$)$_4$), 2.12 (t, $^3J_{PH}$ = 4.4 Hz, 3H, Pd–C*H*$_3$), 1.54 (vt, 36H, J_{P-H} = 6.4 Hz, C(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, RT): δ 64.4 (s). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, RT): δ 162.1 (q, 38 Hz, *ipso*-Ar, B(Ar$_F$)$_4$), 135.2 (*o*-Ar, B(Ar$_F$)$_4$), 128.8 (q, 31 Hz, *m*-Ar, B(Ar$_F$)$_4$), 125.0 (q, 273 Hz, *C*F$_3$, B(Ar$_F$)$_4$), 117.9 (*p*-Ar, B(Ar$_F$)$_4$), 40.7 (vt, J_{PC} = 4.1 Hz, *C*Me$_3$), 33.0 (*C*H$_3$), 5.7 (Pd–*C*H$_3$). Anal. calcd for $C_{57}H_{69}BF_{24}P_2Pd$: C, 49.28; H, 5.01. Found: C, 49.37; H, 4.93.

3-SbF$_6$. In a Schlenk flask precooled to 0 °C [(cod)Pd(Me)(thf)][SbF$_6$] (0.27 mg, 0.5 mmol) and P*t*Bu$_3$ (0.202 g, 1 mmol) were dissolved in 3 mL of CH$_2$Cl$_2$. The yellow-green solution was stirred for 5 min at 0 °C and pentane (20 mL) was added. On pentane addition the yellow-green product precipitated out of solution. The mother liquor was decanted and the product was dried under dynamic vacuum. Yield: 0.25 g (0.33 mmol, 66%). Complex **3**-SbF$_6$ was less stable in CH$_2$Cl$_2$ or THF solution and slow degradation was observed accompanied by the formation of metallic Pd. Single crystals were grown by slow pentane diffusion into a concentrated CH$_2$Cl$_2$ solution at −30 °C. Anal. calcd for $C_{25}H_{47}F_6P_2PdSb$: C, 39.41; H, 7.54. Found: C, 39.22; H, 7.32.

Computational details

All DFT calculations employed the long-range dispersion-corrected Grimme's functional (B97D)[30] as implemented in Gaussian 09[47] and no symmetry restrictions were imposed (C_1). C, H, and P were represented by an all-electron 6-311G(d,p) basis set, whereas the Stuttgart–Dresden basis set-pseudo relativistic effective core potential was used for Pd.[48,49] The nature of the extrema (minima) was established with analytical frequency calculations. The zero point vibration energy (ZPE) and entropic contributions were estimated within the harmonic potential approximation. The Gibbs free energy, ΔG, was calculated for T = 298.15 K and 1 atm. Geometrical parameters were reported within an accuracy of 10^{-3} Å and 10^{-1} degrees.

Acknowledgements

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