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Effect of Pnictogen Ligand Substitution on a Tripalladium Ditropylium Core

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A combination of multinuclei NMR, UV−vis spectroscopy, and single crystal X-ray diffraction was used to characterize a new series of tripalladium ditropylium sandwich complexes $[Pd_3Tr_2(E)_3][BF_4]_2$ (E = PPh_3, $AsPh_3$, and $SbPh_3$ and PEt_3). Ligand substitution leads to a systematic shift of the ^{1}H and ^{13}C NMR tropylium resonances and is correlated with the electron donating properties of the substituent group. Replacement of the ligand increases the palladium-pnictogen bond length in the order P < As < Sb; however, this only slightly alters the internal Pd−Pd bond lengths, supporting the hypothesis that there are only weak Pd−Pd bonding interactions.

Introduction

Stable sandwich complexes of most of the transition metals have been known for some time; however, sandwich complexes of the platinum group metals are relatively rare. Allegra et al. provided the first example of a platinum group sandwich complex in 1965 when a binuclear complex with two palladium atoms coordinated between two benzene rings was reported.[1,2] In 2003 Kloo and co-workers reported a series of dimeric palladium and platinum sandwich complexes, but the instability of these compounds prevents additional investigations of their material properties.[3,4] Other dimetallic and trimetallic complexes of palladium with coordinated arene rings have been reported, and these complexes can have catalytic activity in amination and other reactions.[5−9] These complexes typically have a formal bond between each palladium center.

In 2006, a stable trimetallic sandwich complex consisting of three palladium atoms coordinated between two tropylium ($C_7H_7^+$, Tr) cations was reported by Murahashi et al.[10−14] Although triangular complexes of the group 10 elements have been well studied, they lack the coordinated arene ring characteristic of true sandwich complexes.[15,16] The interesting geometric and electronic characteristics of this new type of trimetallic complex may allow for unique catalytic effects or material properties. Combining small discrete clusters with select linker units may be a method for the creation of well-defined, two-dimensional "super-sandwich" structures with a range of modifiable electronic and structural properties analogous to those displayed by one-dimensional "molecular wires".[17,18] The catalytic activity of these complexes is also under investigation.[19]

Recently we demonstrated that the synthesis of tripalladium ditropylium complexes is general for a wide range of ligands (Scheme 1) and that simple ligand substitution strongly modifies the physical properties of the final complex.[20] These anionic complexes are simple to prepare and are stable to oxygen, moisture, and heat. In addition, these complexes possess unexpected reactivity that includes the ability to form

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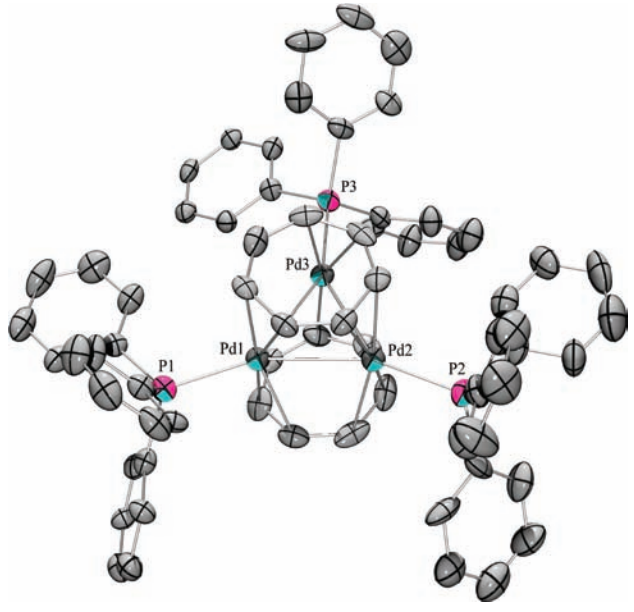
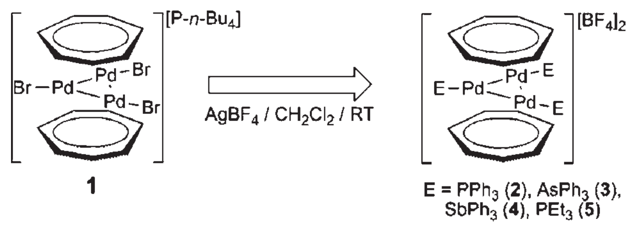


Figure 1. ORTEP plot of **2** at 30% probability level with hydrogen atoms and anions omitted.

Scheme 1. Synthesis of $[Pd_3Tr_2(E)_3][BF_4]_2$ and Numbering Scheme



a new type of one-dimensional halogen-linked polymers of general formula $[Pd_3Tr_2X_2]_n$ (X = Cl, Br, I).

One important question regarding the $[Pd_3Tr_2]^{2+}$ complexes concerns the degree of interaction between the individual palladium centers. Although the palladium–palladium distances in $[Pd_3Tr_2X_3]^-$ (X = Cl, Br, or I) are well within the sum of the van der Waals radii, the natural bond orbital (NBO) bond order was calculated by Murahashi et al. as zero for all Pd–Pd pairs.[10] Density functional theory (DFT) calculations carried out by the same authors indicated the bond order between Pd–Pd pairs to be slightly greater, in the range of 0.282 to 0.258. This is attributed to a small number of donating and back-donating interactions; the degree of Pd–Pd interaction may potentially be observed as changes in the internal Pd–Pd distances upon ligand substitution around the $[Pd_3Tr_2]^{2+}$ core. Despite the lack of significant Pd–Pd interactions, the $[Pd_3Tr_2]^{2+}$ core is nevertheless remarkably robust, and the ease of formation of substituents on the $[Pd_3Tr_2]^{2+}$ core prompts us to consider its utility as the platform for the exploration of substituent effects. Understanding the effects of the substituents on the two-dimensional $[Pd_3Tr_2X_2]_n$ polymers will also illuminate the electronic properties of these molecules and aid in the development of new low-dimensional materials. We report herein the synthesis and characterization of a series of homoleptic tripalladium sandwich complexes with pnictogen substituents.

Results and Discussion

Synthesis of the Pnictogen Complexes. This group has previously reported the synthesis of $[Pd_3Tr_2Br_3][PPh_4]$ via the reaction of $Pd_2(dba)_3 \cdot CHCl_3$, $[C_7H_7][BF_4]$, and excess PPh_4Br in dichloromethane.[20] Although the product crystallizes from solution upon slow evaporation of the solvent, the utility of this complex is limited because it must be separated from excess, co-precipitated PPh_4Br. Recent improvements upon the original procedure include replacement of PPh_4Br with P-*n*-Bu_4Br which allows for removal of the excess reagent upon trituration with diethyl ether to give the pure product $[Pd_3Tr_2Br_3]$[P-*n*-Bu_4] **1** in high yield. This modified synthesis may be conducted in high yield on a multigram scale. The formation of $[Pd_3Tr_2Br_3]^-$ may be monitored by ion-trap mass spectrometry and is essentially complete within 60 min.

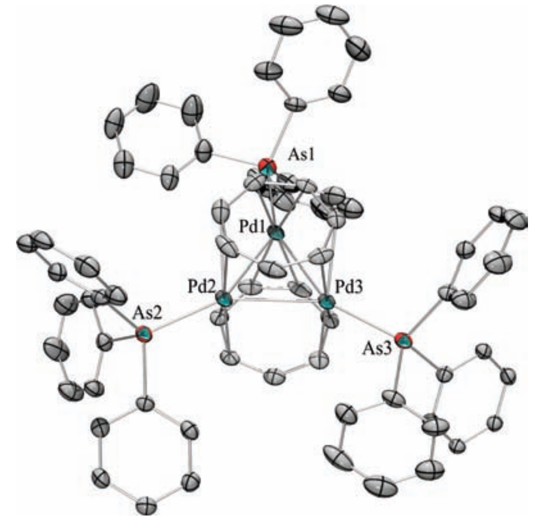


Figure 2. ORTEP plot of **3** at 30% probability level with hydrogen atoms and anions omitted.

The synthesis of $[Pd_3Tr_2(PPh_3)_3][BF_4]_2$ **2** by treatment of $[Pd_3Tr_2Cl_3][PPh_4]$ with $AgBF_4$ in the presence of an excess of PPh_3 has also been previously reported.[10] The reaction of **1** with $AgBF_4$ in the presence of an excess of $AsPh_3$ or $SbPh_3$ leads to formation of $[Pd_3Tr_2(AsPh_3)_3][BF_4]_2$ **3** and $[Pd_3Tr_2(SbPh_3)_3][BF_4]_2$ **4**, respectively, as brightly colored solids in good yield. Fragile needle crystals of **2** were obtained by repeated solvent evaporation of *tert*-butyl methyl ether (TBME) into a saturated dichloromethane solution at −20 °C. Crystals of **3**, **4**, and **5** were grown by vapor diffusion of diethyl ether or TBME into a saturated dichloromethane solution. Molecular structures of **2**, **3**, **4**, and **5** as determined via single-crystal X-ray diffraction studies are shown in Figures 1, 2, 3, and 4, respectively. All three molecules adopt the trinuclear sandwich complex motif, and their general features are similar to those reported previously for $[Pd_3Tr_2Br_3][PPh_4]$.[20] As synthesis of the different pnictogen donor complexes and examination of the internal bond lengths and angles was a key objective, PPh_3 was replaced with the more soluble PEt_3 ligand to give $[Pd_3Tr_2(PEt_3)_3][BF_4]_2$ **5** (Figure 3). Attempts to synthesize the nitrogen analogue $[Pd_3Tr_2(NPh_3)_3][BF_4]_2$ using the same methodology were unsuccessful and may be attributed to the greater difference in absolute hardness between the zerovalent palladium and the NPh_3 ligand. Complexes **1**–**5** were characterized by multinuclei NMR, UV–vis spectroscopy, and elemental analysis.

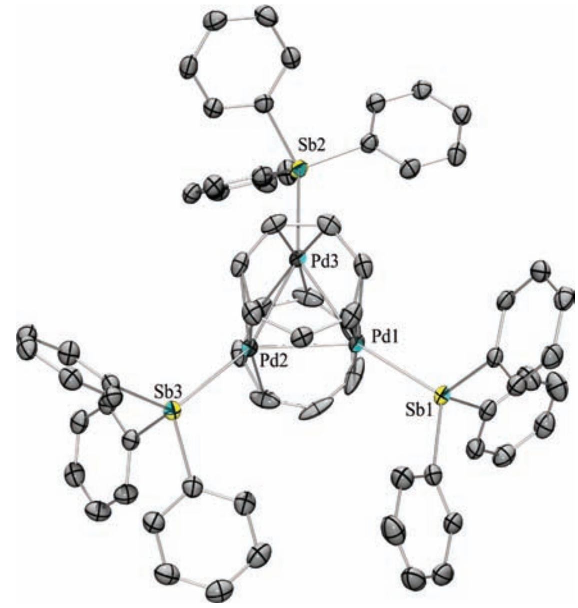


Figure 3. ORTEP plot of **4** at 50% probability level with hydrogen atoms and anions omitted.

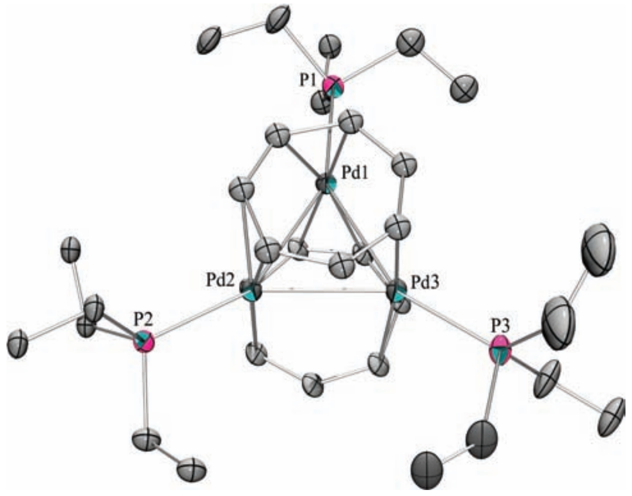


Figure 4. ORTEP plot of one of the unique $[Pd_3Tr_2(PEt_3)_3]^{2+}$ units in **5** at 30% probability level with hydrogen atoms omitted.

Table 1. ^{1}H and ^{13}C NMR Shifts for the Tropylium Cation Resonance in Complexes **2**−**5**

complex	^{1}H NMR ($CDCl_3$)	^{13}C NMR ($CDCl_3$)
2	4.27	62.3
3	4.40	66.6
4	4.81	70.0
5	4.50	67.1

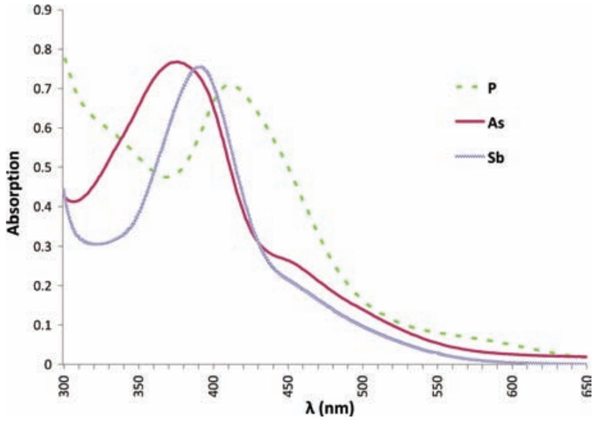


Figure 5. UV−visible spectra of **2**−**5**.

Spectroscopic Characterization of the Pnictogen Complexes. The results of ^{1}H and ^{13}C NMR studies of the pnictogen complexes **2**−**5** are summarized in Table 1, with the resonance of the tropylium cation displaying a steady progression to higher frequencies following the order P < As < Sb. This is not unexpected as the σ-donor/π-acceptor ratio for these ligands follows the order $SbPh_3$ > $AsPh_3$ > PPh_3 resulting in an electronic deshielding of the tropylium ring. A greater influence is exerted on the NMR shifts upon replacement of the R group, with ethyl having a greater σ-donor/π-acceptor ratio than phenyl. The ^{1}H and ^{13}C tropylium resonances therefore serve as a sensitive measure of the electronic effects of the ligand on the $[Pd_3Tr_2]^{2+}$ core. ^{31}P NMR studies on **2** and **5** indicate a singlet resonance at 18.83 ppm and 7.31 ppm, respectively. The presence of significant interaction between the palladium atoms should allow for potential ^{31}P−^{31}P interactions. The absence of any observed coupling suggests minimal Pd−Pd interactions; however, absence of coupling could also be due to equivalent phosphorous environments.

The UV−visible spectrum of **1** is identical to the analogous $[Pd_3Tr_2Br_3][PPh_4]$ complex as well as the other halogenated complexes, demonstrating the minimal influence of the countercation or equatorial ligands on the absorption spectra. The results of the UV−vis spectroscopic studies on complexes **2**− **5** are summarized in Figure 5, and the complexes display a single large absorption at 410 nm (**2**), 390 nm (**4**), and 374 nm (**3**). The replacement of the electron-rich halides with the neutral pnictogen ligands leads to a larger HOMO−LUMO gap and a shift of λ_{max} to higher energies. There is a noticeable decrease in solubility of the complexes in the order of PPh_3 < $AsPh_3$ < $SbPh_3$.

X-ray Diffraction Studies of the Pnictogen Complexes. The results of single crystal X-ray diffraction studies on compounds **2**−**5** are summarized in Table 2, and selected bond lengths and angles are collected in Table 3. The low solubility of **2** in chlorinated solvents gave only small, fragile crystals, and synchrotron radiation was needed for data collection of **2** and **4**. Refinement of **5** (the unit cell of which contains 24 separate species, 5 complexes, 10 counterions, and 9 solvent molecules) was particularly challenging, and even with long (60 s) exposures, diffraction was only observed up to a resolution of 1 Å and the data set was truncated at this point. Hence for this structure the final residuals are somewhat higher than usual. Repeated crystallizations of **5** did not yield crystals of higher quality or stability. Further details are given in the Experimental Section.

Previous work on the tripalladium ditropylium motif has revealed interesting structural characteristics, and the compounds described here are no exception.[20] In all compounds the $[Pd_3Tr_2]^{2+}$ core is retained with a near equilateral triangle arrangement of Pd−Pd bonds. Although in **2** and **3** the Pd−Pd bond lengths vary by ~0.05 Å, this does not significantly alter the internal

Table 2. Crystal data for Compounds **2**−**5**[a]

	2	**3**	**4**	**5**
formula	$C_{68}H_{59}B_2F_8P_3Pd_3$	$C_{68}H_{59}As_3B_2F_8Pd_3$	$C_{68}H_{59}Sb_3B_2F_8Pd_3$	$C_{169}H_{313}B_{10}Cl_{18}F_{40}P_{15}Pd_{15}$
moiety formula	$C_{68}H_{59}As_3Pd_3{}^{2+}\cdot 2BF_4{}^-$	$C_{68}H_{59}As_3Pd_3{}^{2+}\cdot 2BF_4{}^-$	$C_{68}H_{59}Sb_3Pd_3{}^{2+}\cdot 2BF_4{}^-$	$5C_{68}H_{59}P_3Pd_3{}^{2+}\cdot 10BF_4{}^-\cdot 9CH_2Cl_2$
formula weight	1461.88	1593.73	1734.22	5911.94
radiation type	synchrotron, λ = 0.7749 Å	Cu Kα	synchrotron, λ = 0.7749 Å	Mo Kα
space group	monoclinic, $I2/a$	monoclinic, $C2/c$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a, Å	14.9823(9)	32.5623(12)	15.7531(13)	15.047(6)
b, Å	27.0746(15)	27.1922(10)	14.4881(12)	17.647(7)
c, Å	30.441(2)	15.4222(6)	27.293(2)	43.937(17)
α, deg	90	90	90	84.523(5)
β, deg	96.119(4)	111.955(2)	100.617(12)	81.124(5)
γ, deg	90	90	90	88.128(5)
V, Å^3	12277.7(13)	12665.1(8)	6122.4(9)	11473(7)
Z	8	8	4	2
ρ_{calc}., g cm^{-3}	1.582	1.672	1.881	1.711
μ, mm^{-1}	1.013	9.076	2.233	1.534
T, K	150(2)	100(2)	100(2)	120(2)
reflections collected	34243	31993	76188	52503
independent reflections	5456	10513	15166	24033
final R indices [$I > 2\sigma(I)$]	R1 = 0.0482, wR2 = 0.1201	R1 = 0.0439, wR2 = 0.1167	R1 = 0.0325, wR2 = 0.0716	R1 = 0.1061, wR2 = 0.2657

[a] Programs used. Data collection and reduction: SMART, SAINT, and APEX2.[29] Absorption correction: SADABS.[30] Structure solution and refinement: SHELXTL.[31] Molecular graphics: ORTEP-3 for Windows.[32]

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes **2**−**5**

2		**3**	
Pd(1)−Pd(2)	2.8208(11)	Pd(1)−Pd(2)	2.7957(5)
Pd(2)−Pd(3)	2.8305(12)	Pd(2)−Pd(3)	2.8450(5)
Pd(3)−Pd(1)	2.8678(12)	Pd(3)−Pd(1)	2.7927(5)
Pd(1)−P(1)	2.389(3)	Pd(1)−As(1)	2.4676(7)
Pd(2)−P(2)	2.385(3)	Pd(2)−As(2)	2.4736(7)
Pd(3)−P(3)	2.384(3)	Pd(3)−As(3)	2.4816(7)
Pd(2)−Pd(1)−Pd(3)	59.67(3)	Pd(2)−Pd(1)−Pd(3)	61.206(14)
Pd(1)−Pd(2)−Pd(3)	60.99(3)	Pd(1)−Pd(2)−Pd(3)	59.346(13)
Pd(2)−Pd(3)−Pd(1)	59.34(3)	Pd(2)−Pd(3)−Pd(1)	59.448(13)
4		**5**[a]	
Pd(1)−Pd(2)	2.8170(4)	Pd(1)−Pd(2)	2.820(3)
Pd(2)−Pd(3)	2.8046(5)	Pd(2)−Pd(3)	2.872(2)
Pd(3)−Pd(1)	2.7892(4)	Pd(3)−Pd(1)	2.812(3)
Pd(1)−Sb(1)	2.6062(4)	Pd(1)−P(1)	2.364(7)
Pd(2)−Sb(2)	2.6060(4)	Pd(2)−P(2)	2.361(6)
Pd(3)−Sb(3)	2.6121(4)	Pd(3)−P(3)	2.373(7)
Pd(2)−Pd(1)−Pd(3)	60.033(11)	Pd(2)−Pd(1)−Pd(3)	61.33(6)
Pd(1)−Pd(2)−Pd(3)	59.491(11)	Pd(1)−Pd(2)−Pd(3)	59.21(6)
Pd(2)−Pd(3)−Pd(1)	60.476(10)	Pd(2)−Pd(3)−Pd(1)	59.46(6)

[a] For **5** a single $[Pd_3Tr_2(PEt_3)_3]^{2+}$ unit has been listed to give representative bond lengths and angles.

Pd−Pd−Pd angles. The tropylium ring is planar in all the complexes characteristic of the expected aromaticity and overall positive charge. Comparison of the bond distances reveals a distinct trend of increasing Pd−E bond length (E = P, As or Sb) that follows the trend Pd−Sb > Pd−As > Pd−P. The Pd−P bond lengths of **2** (PPh_3) are slightly longer (~0.02 Å) than in **5** (PEt_3) and may be due to differences in π-back-donation. Although the structure of **5** has five crystallographically unique $[Pd_3Tr_2(PEt_3)_3]^{2+}$ units and thus a range of Pd−P bond lengths (2.358(6) Å to 2.399(7) Å), all the Pd−P bonds are considerably shorter than the analogous Pd−As and Pd−Sb bonds. This trend is expected upon replacement of the lighter pnictogens for the heavier analogues. Although ligand replacement does not significantly affect the internal angles of the $[Pd_3Tr_2]^{2+}$ unit, the Pd−Pd bond lengths increase slightly but observably (greater than three standard deviations) with PPh_3 ~ PEt_3 > $AsPh_3$ > $SbPh_3$. Despite caution necessitated by higher refinement residuals the average length of all 15 unique Pd−Pd bonds in **5** is still significantly longer than for those of **3** and **4**. The Pd−Pd bond distances in **2**−**5** are also significantly longer (~0.05 Å) than those observed in the $[Pd_3Tr_2X_3][PPh_4]$ (X = Cl, Br and I) series of complexes, and this effect is likely due to the removal of electron density upon replacing anionic halide ligands with the neutral pnictogen ligands. The ability of the pnictogen ligands to accept electron density from the metal into empty 3d orbitals is also expected to decrease the electron density on the metal and thereby weaken any Pd−Pd bonding interaction. No significant change is observed in the distance between the plane formed by the palladium atoms and the plane defined by the coordinated tropylium rings in complexes **2**− **5**. Replacement of the equatorial ligands with aryl and alkyl pnictogen ligands with differing σ-donor and π-acceptor properties can therefore permit the "tuning" of the internal Pd−Pd distances. It may also be possible to mix aryl and alkyl pnictogen ligands to give a diverse range of complexes.

In the current series of complexes there is significant steric crowding around the $[Pd_3Tr_2]^{2+}$ core, and this is most prominent in **2** because of the shorter Pd−P distance and rigid phenyl rings. The through-space P−P distances in **2** (6.810(4) Å, 6.868(4) Å, and 7.192(4) Å) suggests that it may be possible to replace two PPh_3 ligands with a single bidentate ligand such as commercially available bis(diphenylphosphino)hexane (dpph) (P−P distance = 8−9 Å, depending upon conformation).[21,22]

Although many examples of complexes with Pd−P bonds have been reported, fewer examples of complexes with Pd−As appear in the literature and complexes with Pd−Sb bonds are rarer still. Examples of palladium(II)−triphenylstibine complexes have been reported previously; however, a search of the Cambridge Structural Database (CSD, version 5.30 plus four updates)[23] returns only two structures reported as palladium(0)-triphenylstibine complexes from a single journal article.[24] In comparison with **4**, these systems possess longer Pd−Pd distances (2.892 Å and 3.012 Å vs **4** 2.7892(4) Å to 2.8170(4) Å), shorter Pd−Sb bond lengths (2.508 Å and 2.473 Å vs **4** 2.6060(4) Å to 2.6121(4) Å) and have an overall electronic configuration more compatible with isolated Pd^{2+} centers.[25] Comparison of the Pd−As bond lengths in **3** (2.4676(7), 2.4736(7), and 2.4816(7) Å) with those of a series of divalent palladium complexes shows a lengthening of the Pd−As bond upon coordination to a lower-valent metal center. Clegg et al. have previously demonstrated that even in complexes with very short Pd−Pd distances such as $[Pd_2(mhp)_4]$ (mhp = 6-methyl-2-oxypyridine, Pd−Pd = 2.546 Å) there can be a formal bond order of zero between palladium centers.[26] Therefore, the structure of **4** can be considered to be the first unambiguous report of a palladium(0)−antimony bond.

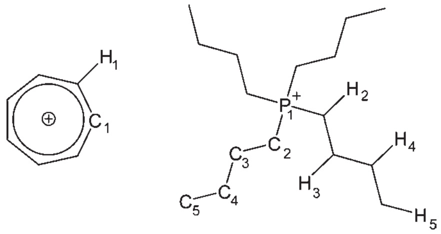
Conclusions

This series of pnictogen-palladium complexes represents an important contribution to the understanding of the new class of trimetallic sandwich complexes and allows for spectroscopic and structural comparisons. The simplicity and extent of metathesis reactions that may be carried out on the $[Pd_3Tr_2]^{2+}$ motif makes the reaction a powerful method for the introduction of a range of functional groups. These studies indicate that the NMR properties and internal bond lengths are influenced by the equatorial ligands, and this may provide a way to engineer the Pd−Pd bond lengths. The ease of substitution with pnictogen ligands will allow the incorporation of bidentate pnictogen ligands such as bis(diphenylphosphino)hexane (dpph) and other multidentate ligands, and is currently underway.

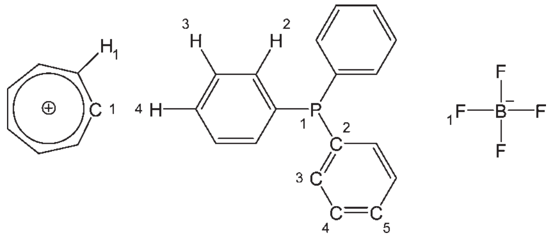
Experimental Section

All experiments were performed under an Ar atmosphere using standard Schlenk techniques. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{19}F NMR spectra were recorded on a 400 MHz (Varian Mercury) instrument, and the chemical shifts were referenced to the residual resonances of the deuterated solvents. Elemental analyses were performed by Robertson Microlit Laboratories Inc. of Madison, New Jersey, and mass spectra were collected on a Varian 500-MS ion-trap mass spectrometer. Dichloromethane, *tert*-butyl methyl ether (TBME) and diethyl ether were purified according to standard procedures. $Pd_2(dba)_3 \cdot CHCl_3$ (dba = dibenzylideneacetone) was prepared according to the method of Ukai et al.[27] The chemicals P-*n*-Bu_4Br, $[C_7H_7][BF_4]$, PPh_3, PEt_3, $AsPh_3$, $SbPh_3$, and $AgBF_4$ were purchased from the Sigma Aldrich Corporation and used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

Synthesis of $[Pd_3Tr_3Br_3]$[P-*n*-Bu_4] (1). To a solution of $[C_7H_7][BF_4]$ (138 mg, 0.77 mmol) and P-*n*-Bu_4Br (982 mg, 2.90 mmol) in CH_2Cl_2 (100 mL), $Pd_2(dba)_3 \cdot CHCl_3$ (600 mg, 0.58 mmol) was added, and the solution was stirred for 30 min. The solution was filtered then reduced in volume (30 mL), and diethyl ether (100 mL) was added, yielding pinkish-brown precipitates. The precipitate was collected and dried in vacuo. Yield based on Pd: 313.3 mg (81.0%). Anal. Calcd. For $C_{30}H_{50}Br_3PPd_3$: C, 36.01; H, 5.04; N, 0.00. Found: C, 35.93; H, 4.82; N, < 0.02. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 4.74 (s, 14H, H_1), 2.20 (m, 8H, H_2), 1.53 (m, 16H, H_3-H_4), 0.99 (t, 12H, H_5). $^{13}C\{^1H\}$-NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 73.17 (s, C_1), 22.37 (d, J = 15.2 Hz, C_3), 22.13 (d, J = 4.6 Hz, C_4), 17.37 (d, J = 47.3 Hz, C_2), 11.88 (s, C_5). $^{31}P\{^1H\}$-NMR (161.9 MHz, $CDCl_3$, 25 °C): δ 34.20 (s, P_1). MS (ESI) m/z 742.6 $[M - PBu_4^+]$.



Synthesis of $[Pd_3Tr_2(PPh_3)_3][BF_4]_2$ (2). To a solution of **1** (200 mg, 0.20 mmol) and PPh_3 (786.9 mg, 3.00 mmol) in CH_2Cl_2 (100 mL), $AgBF_4$ (389.4 mg, 2.00 mmol) was added, and the solution was stirred for 1 h. The solution was filtered leaving a brownish-gray precipitate and a dark reddish-brown filtrate. The filtrate was reduced in volume to ~30 mL and diethyl ether (100 mL) was added, yielding a bright orange precipitate. The solution was filtered, and the precipitate was washed with excess diethyl ether (2 × 25 mL) then dried in vacuo. Yield: 216.7 mg (74.1%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.53 (s, H, H_4), 7.36 (s, 14H, H_3), 4.27 (s, 14H, H_1). $^{13}C\{^1H\}$-NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 136.4 (s, C_5), 130.5 (s, C_4), 130.1 (s, C_3), 62.3 (s) C_1. $^{31}P\{^1H\}$-NMR (161.9 MHz, $CDCl_3$, 25 °C): δ 18.83 (s, P_1). ^{19}F NMR (376.2 MHz, $CDCl_3$, 25 °C): δ −158.73 (s, F_1). UV−visible [CH_2Cl_2 λ_{max} (nm) 410.1 (15.2 × 10^3)].



Synthesis of $[Pd_3Tr_2(AsPh_3)_3][BF_4]_2$ (3). The product was synthesized using an analogous method to **2** yielding a dull

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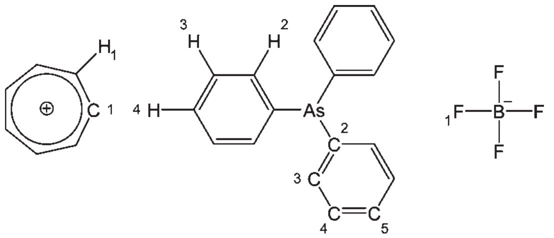
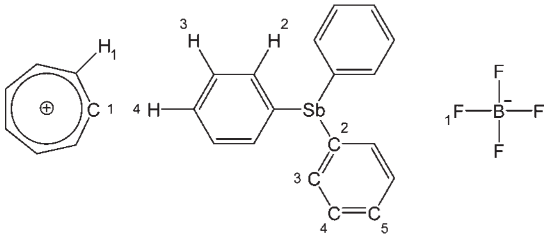
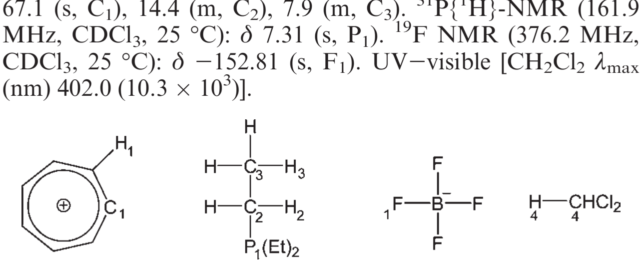
orange powder. The complex was recrystallized from dichloromethane and *tert*-butyl methyl ether. Yield: 283.3 mg (88.9%). Anal. Calcd. For $C_{68}H_{59}As_3B_2F_8Pd_3$: C, 51.24; H, 3.73; N, 0.00. Found: C, 51.67; H, 3.52; N, <0.02. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.39 (s, 9H, H_4), 7.10−7.22 (s, 32H, H_2-H_3), 4.40 (s, 14H, H_1). $^{13}C\{^1H\}$-NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 127.7 (s, C_5), 124.2 (s, C_4), 66.6 (s, C_1). ^{19}F NMR (376.2 MHz, $CDCl_3$, 25 °C): δ −158.07 (s, F_1). UV−visible [CH_2Cl_2 λ_{max} (nm) 441.1 (6.3 × 10^3)].



Synthesis of [$Pd_3Tr_2(SbPh_3)_3$][BF_4]$_2$ (4). The product was synthesized using an analogous method to **2**, yielding a brilliant orange powder that was recrystallized from dichloromethane and *tert*-butyl methyl ether. Yield: 288.8 mg (83.5%). Anal. Calcd. For $C_{68}H_{59}B_2F_8Pd_3Sb_3$: C, 47.09; H, 3.43; N, 0.00. Found: C, 46.58; H, 3.52; N, <0.02. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.42 (t, 9H, H_4), 7.37 (m, 32H, H_2-H_3), 4.81 (s, 14H, H_1). $^{13}C\{^1H\}$-NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 136.10 (s, C_5), 130.6 (s, C_4), 130.1 (s, C_3), 70.0 (s, C_1). ^{19}F NMR (376.2 MHz, $CDCl_3$, 25 °C): δ −151.01 (s, F_1). UV−visible [CH_2Cl_2 λ_{max} (nm) 449.0 (2.3 × 10^3)].



Synthesis of [$Pd_3Tr_2(PEt_3)_3$][BF_4]$_2$·CH_2Cl_2 (5). The product was synthesized using an analogous method to **2**, yielding a dark burgundy colored powder that was recrystallized from dichloromethane and diethyl ether. Yield: 78.4 mg (64.9%). Anal. Calcd. For $C_{33}H_{61}B_2Cl_2F_8P_3Pd_3$: C, 35.56; H, 5.52; N, 0.00. Found: C, 35.83; H, 5.44; N, <0.02. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 5.31 (s, 2H, H_4), 4.50 (s, 14H, H_1), 1.75 (m, 18H, H_2), 0.78 (m, 27H, H_3). $^{13}C\{^1H\}$-NMR (100.5 MHz, $CDCl_3$, 25 °C): δ 67.1 (s, C_1), 14.4 (m, C_2), 7.9 (m, C_3). $^{31}P\{^1H\}$-NMR (161.9 MHz, $CDCl_3$, 25 °C): δ 7.31 (s, P_1). ^{19}F NMR (376.2 MHz, $CDCl_3$, 25 °C): δ −152.81 (s, F_1). UV−visible [CH_2Cl_2 λ_{max} (nm) 402.0 (10.3 × 10^3)].



X-ray Crystallography

Single crystal X-ray diffraction data were measured on Bruker SMART APEXII (**2** and **4**), Bruker Kappa APEXII DUO (**3**), or Bruker SMART 1000 (**5**) diffractometers. In all cases hydrogen atoms were placed geometrically, with C−H distances in the range 0.95−0.99 Å (according to C-atom hybridization) and refined with $U_{iso}(H) = 1.2U_{eq}(C)$ ($U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups). For **2** with a 30 s synchrotron radiation exposure time data could only be observed to a resolution of 1.05 Å, beyond this resolution $R\sigma \geq 25\%$; the data-to-parameter ratio is reduced as a result. During refinements of **2** and **3** it was not possible to model some of the BF_4^- counterions, which were disordered over symmetry elements, with discrete atoms, and so electron density pertaining to the counterions was removed with the SQUEEZE routine of PLATON.[28] Obtaining a satisfactory crystal structure of **5** proved to be a serious challenge. Repeated recrystallization by diffusion of diethyl ether into a dichloromethane solution always resulted in small fragile dark red crystals which were observed to lose solvent rapidly when removed from the mother liquor. Even with long (60 s) exposures diffraction was only observed up to a resolution of 1 Å, and the data set was truncated at this point, giving a reduced data-to-parameter ratio. Hence for this structure final residuals are somewhat higher than usual. The asymmetric unit of **5** contains 5 [$Pd_3Tr_2(PEt_3)_3$]$^{2+}$ dications, 10 [BF_4]$^-$ anions, and 9 molecules of CH_2Cl_2 solvent. Although the structure was solved easily by direct methods, identifying the five triangular Pd_3 units, and successive Fourier maps clearly identified the ligands, counterions, and solvent molecules, this very large number of parameters, combined with poor diffraction, make for a challenging and lengthy refinement. Internal bond distances in the anions and solvent molecules were controlled using soft restraints to target values. Some of the PEt_3 ligands also required geometric restraints, and although some of the ellipsoids strongly indicate that a disorder model should be used, the overall refinement became unstable as a result. Similarity restraints on the anisotropic displacement ellipsoids were necessary for the counterions and some solvent molecules. One of the dichloromethane molecules (containing Cl17 and Cl18) was refined with partial occupancy (86% occupied), consistent with the rapid desolvation observed. However, the chemical formulas and formula weight have all been calculated assuming 100% occupancy of this molecule.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compounds **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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