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Synthesis and Characterization of Thiolato-Bridged Titanium−Platinum and −Palladium Heterobinuclear Complexes. Molecular Structure of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SPh)_2Pd(C_6F_5)_2]$

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A series of titanium−platinum and −palladium heterobinuclear compounds with double thiolato bridges, $[(\eta^5\text{-}C_5H_4R')_2Ti(\mu\text{-}SR)_2M(C_6F_5)_2]$ (R′ = H, $SiMe_3$; R = Ph, C_6F_5; M = Pd, Pt), has been prepared. The crystal structure of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SPh)_2Pd(C_6F_5)_2]$ has been established by single-crystal X-ray crystallography: the complex crystallizes in the monoclinic system in space group $P2_1/c$; $a = 10.237$ (2) Å; $b = 14.635$ (3) Å; $c = 27.651$ (6) Å; $\beta = 90.83$ (2)°; $Z = 4$; and $R = 0.056$. The titanium atom is in pseudotetrahedral coordination environment, whereas the palladium is square-planar. The phenyl groups on the sulfur atoms adopt an endo (*syn*) arrangement with respect to the central $Ti-S_2-Pd$ core.

Introduction

The synthesis and study of homo- and heterobinuclear complexes have been the subject of active research over the past few years. Interest in this area is due principally to the idea that two metal atoms in close proximity could react in a cooperative manner with substrate molecules.[1] Recently, special attention has been focused upon early−late transition metal heterobimetallic complexes[2] because of their potential ability to promote activation of polar molecules, such as carbon monoxide. In addition, these complexes have been studied in order to gain understanding of the phenomenon of "strong metal−support interactions (SMSI)" in heterogeneous catalysis.[3] Several synthetic routes to complexes containing both an early and a late transition metal have been described and recently reviewed. [4] Due to the propensity of sulfur to form M(μ-SR)-M′ bridges[5] one approach to the synthesis of such species has involved the use of S-functionalized (thiolates, pendant phosphinethiolates, macrocyclic thiolates) early metal complexes as metalloligands to a suitable late transition metal complex. Thus, there have been extensive structural studies of such species, especially those involving a d^{10} late transition metal as a receiver with a d^0 early metal;[2ek,6] these species have attracted additional interest on account of the nature of the dative ($d^{10}\rightarrow d^0$) metal interaction and conformational aspects.[7] By contrast, very few examples of related thiolato-bridged complexes containing a d^8 late transition metal and a d^0 early one have hitherto been prepared.[6f,8] In some cases, attempts of sulfur complexation of a d^8 late transition metal [Ni(II), Pd(II)][2k,6c,f] only produces late metal thiolate aggregates. It has been pointed out by Stephan and co-workers [2k] that the Lewis acidity of the d^8 late metal may act to destabilize the Ti−S bonds, resulting in thiolate transfer reactions.

As part of our current interest in the chemistry of *cis*-$[M(C_6F_5)_2(THF)_2]$ (M = Pd, Pt; THF = tetrahydrofuran) derivatives,[9] particularly as precursors for the synthesis of polynuclear complexes,[10] we are studying their reactivity toward different types of potential metalloligands. Thus, in this area, we have recently reported the synthesis of the binuclear (d^0−d^8) complex $[Cp_2Ti(\mu\text{-}\eta^1\text{-}C{\equiv}CBu^t)_2Pt(C_6F_5)_2]$[11] by using the bis(alkynyl)titanocene derivative $[Cp_2Ti(C{\equiv}CBu^t)_2]$ as starting

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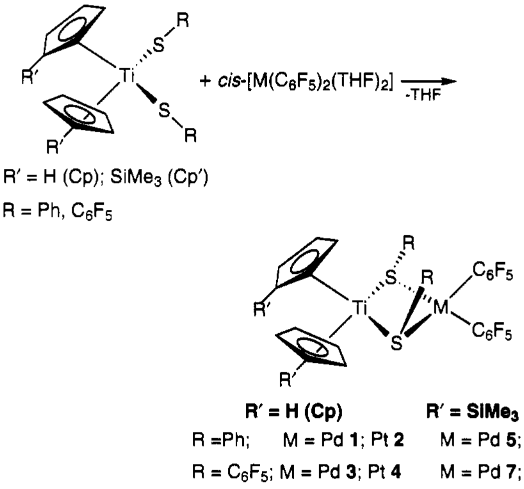
material. In this paper we wish to report the synthesis of titanium–palladium and –platinum heterobinuclear complexes (d^0–d^8) in which the metal centers are linked by means of SPh or SC_6F_5 bridges. The structure of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SPh)_2Pd(C_6F_5)_2]$ (**5**) has been established by single-crystal X-ray diffraction and, to the best of our knowledge, this is the first example of a mixed Ti–Pd compound being structurally characterized.

Results and Discussion

We have previously described the synthesis of some new thiolate derivatives of the type $[(Cp')_2Ti(SR)_2]$[12] (Cp′ = $C_5H_4SiMe_3$) by reacting $[(Cp')_2TiCl_2]$ with thiols in the presence of base. In order to develop also the synthetic potential of these bent metallocene thiolates and with the aim of synthesizing new heterobimetallic Ti–M (M = Pd, Pt) species, we have studied the reactivity of $[(Cp')_2Ti(SR)_2]$ (R = Ph, C_6F_5) and the titanocene analogues $[(Cp)_2Ti(SR)_2]$ (R = Ph, C_6F_5) toward *cis*-$[M(C_6F_5)_2(THF)_2]$. The results of this study are summarized in eq 1. *cis*-$[M(C_6F_5)_2(THF)_2]$ (M = Pd, Pt) reacts with the bent metallocene thiolates $[(\eta^5\text{-}C_5H_4R')_2Ti(SR)_2]$ (R′ = H, $SiMe_3$), yielding the binuclear air-sensitive derivatives $[(\eta^5\text{-}C_5H_4R')_2Ti(\mu\text{-}SR)_2M(C_6F_5)_2]$, in which the thiolate Ti(IV) compound, after displacing the THF ligands of the $[M(C_6F_5)_2(THF)_2]$ substrates, is acting as a metalloligand toward the "$M(C_6F_5)_2$" fragment.



R′ = H (Cp); SiMe₃ (Cp′)
R = Ph, C₆F₅

(1)

R′ = H (Cp)	**R′ = SiMe₃ (Cp′)**
R = Ph; M = Pd **1**; Pt **2**	M = Pd **5**; Pt **6**
R = C₆F₅; M = Pd **3**; Pt **4**	M = Pd **7**; Pt **8**

Elemental analyses, color, yield, and other structural data (IR and ^1H and ^{19}F NMR) are given in the Experimental Section. The conformation of the central $Ti(\mu\text{-}SR)_2M$ core in the binuclear complexes **1**–**8** has been established by single crystal X-ray structure determination of **5** and is consistent with the NMR data.

Structure of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SPh)_2Pd(C_6F_5)_2]$ (5). A drawing of the molecular structure showing the atom numbering scheme is presented in Figure 1. Selected bond lengths and angles are collected in Table 1.

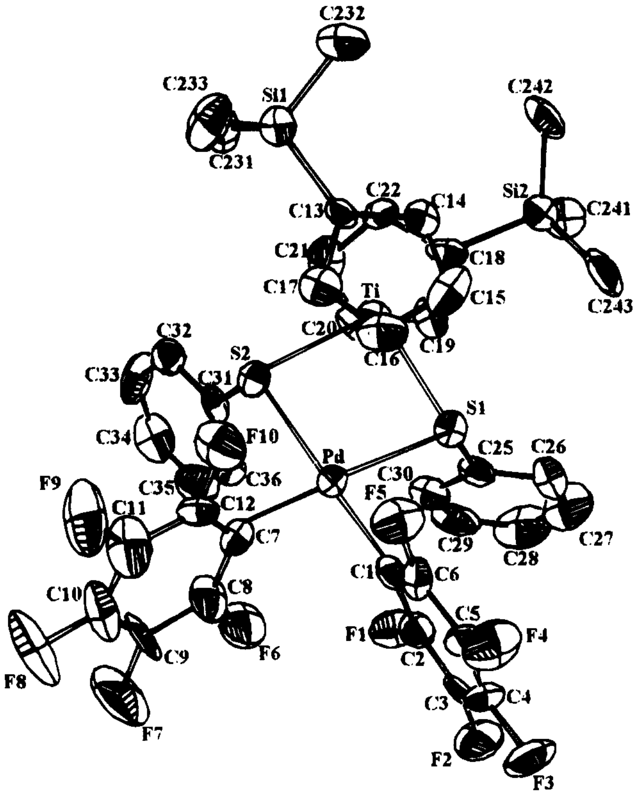


Figure 1. View of the molecular structure of complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SPh)_2Pd(C_6F_5)_2]$ (**5**) with the atomic numbering scheme.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SPh)_2Pd(C_6F_5)_2]$ (**5**)

	Bond Lengths		
Pd–S(1)	2.385 (4)	Pd–S(2)	2.382 (4)
Pd–C(1)	2.03 (2)	Pd–C(7)	2.03 (2)
Ti–S(1)	2.452 (5)	Ti–S(2)	2.462 (5)
S(1)–C(25)	1.76 (2)	S(2)–C(31)	1.77 (2)
Cp1–Ti	2.07 (2)	Cp2–Ti	2.05 (1)
Pd–Ti	3.140 (3)		
	Bond Angles		
C(1)–Pd–C(7)	86.1 (6)	S(2)–Pd–C(7)	88.2 (5)
S(1)–Pd–C(1)	85.9 (4)	S(1)–Pd–S(2)	99.7 (2)
S(1)–Ti–S(2)	95.7 (2)	Pd–S(1)–Ti	80.9 (1)
Ti–S(1)–C(25)	118.4 (6)	Pd–S(1)–C(25)	107.8 (6)
Pd–S(2)–Ti	80.8 (2)	Ti–S(2)–C(31)	118.6 (5)
Pd–S(2)–C(31)	108.4 (6)	Cp1–Ti–Cp2	133 (1)

The titanium atom is located in a pseudotetrahedral coordination environment formed by the two trimethylsilylcyclopentadienyl rings and the two sulfur atoms of the benzenethiolate ligands. The sulfur atoms also bind to the palladium center which completes its distorted square-planar coordination sphere with the C_{ipso} atoms of the two C_6F_5 groups. This geometry is consistent with the formulation of **5** as a Ti(IV)–Pd(II) species.

The Ti–C bond distances [2.34 (1)–2.44 (1) Å] and the centroid (1)–Ti-centroid (2) angle [133 (1)°] are in the usual range found for complexes of this type[2e,k,6c–g,8b,12] with the cyclopentadienyl rings adopting a staggered disposition. The Pd–C distances are similar to the corresponding ones found in other complexes which contain the "*cis*-$Pd(C_6F_5)_2$" fragment,[13] and, as usual, the two pentafluorophenyl rings are forming angles of 87.82 (0.38)° and 110.80 (0.47)°, respectively, with the coordination plane of Pd (the best least squares plane including the Pd center, the two C_{ipso} atoms, and the two sulfur atoms).

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The Ti−S distances [2.462 (5) and 2.452 (5) Å] are similar to those found in related thiolate-bridged early−late heterobimetallic complexes.[2e,k,6d,e,g,8b] In addition, although crystal data for the $(Cp')_2Ti(SPh)_2$ monomer are not available, the Ti−S distances in **5** are longer than those found in other titanocenedithiolates such as $(Cp')_2Ti(SC_6F_5)_2$ [2.438 (2) and 2.431 (2) Å],[12] $Cp_2Ti(SPh)_2$ [2.394 (8) and 2.424 (8) Å],[14] $Cp_2Ti(SEt)_2$ [2.398 (3) and 2.387 (3) Å],[15a] or $Cp_2Ti(SMe)_2$ [2.400 (1) Å][6c,15b] as expected on the basis of thiolate bridging to Pd. The Pd−S distances [2.382 (4) and 2.385 (4) Å] are identical, within experimental error, to those found in the tetranuclear mixed anion $[(C_6F_5)_2Pd(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]^{2-}$ (**A**) [2.387 (3) and 2.391 (2) Å].[10f]

The angles about the core are comparable to those found in other Ti−late-metal thiolate-bridged heterobimetallics. Thus, in concordance with earlier discussions,[16] the S(2)−Ti−S(1) angle [95.7 (2)°] is not very different from those found in simple titanocene dithiolates [$(Cp')_2Ti(SC_6F_5)_2$, 100.6°;[12] $Cp_2Ti(SR)_2$, R = Ph,[14] 99.4°, R = Et,[15a] 93.8°, and R = Me,[6c,15b] 93.7°] suggesting that binding to a second metal does little influence on the S−Ti−S angle. The S(2)−Pd−S(1) angle [99.7 (2)°] is greater than expected for a square-planar Pd center and substantially larger than the corresponding angle observed in anion **A** [S(2)−Pd−S(3) = 79.6 (1)°][10f] but compares well with the S(1)−Rh−S(2) angle found in the isoelectronic (d^0−d^8) species $[Cp_2Ti\{\mu\text{-}S(CH_2)_3PPh_2\}_2Rh]^+$ [100.1 (1)°].[8b] Angles at the bridging sulfur atoms are 80.8 (2)° and 80.9 (1)°. These angles are similar to those found in $[Cp_2Ti\{\mu\text{-}S(CH_2)_3PPh_2\}_2Rh]^+$ [81.5 (1)°],[8b] $[\{Cp_2Ti(\mu\text{-}S(CH_2)_3S)_2TiCp_2\}Ag]^+$ [average 79.6 (4)°],[2e] or in $[Cp_2Ti(\mu\text{-}SMe)_2Mo(CO)_4]$ [82.4 (1)° and 83.2 (1)°][17] and slightly larger than those found in $[Cp_2Ti(\mu\text{-}SMe)_2Cu(NCMe)_2]^+$ [73.6 (1)° and 74.2 (1)°],[6d] $[Cp_2Ti(\mu\text{-}SEt)_2CuL]$ (L = PPh_3, 72.9°; L = PCy_3 74.1 (1)° and 73.8 (1)°],[6e] or $[\{Cp_2Ti(\mu\text{-}SMe)_2\}_2Ni]$ [72.0°][6c] for which dative M → Ti bonding interactions have been suggested. Angles at bridging atoms of about 80° or less have been cited as evidence for metal−metal interaction.[4,8b,17]

The double benzenethiolate bridging system adopts an *endo* (*syn*) conformation. This structural feature is consistent with recent theoretical calculations and previous X-ray studies which seem to confirm a relationship between both the conformation of the bent metallocene thiolate complexes $Cp_2M(SR)_2$ and their heterobimetallic analogues.[7,16] Thus, structural data reveal that free titanocenedithiolates $Cp_2Ti(SR)_2$ adopt an *endo anti* conformation.[6c,12,14,15] On binding to the late metal center, a slight rotation of the SR about the Ti−S bonds explains the observed *endo* (*syn* or *anti*) conformation of the dithiolate moieties in the binuclear systems. Another point of interest is the fact that the phenyl substituents do not lie parallel to each other [dihedral angle 50.41 (0.65)°], as would be expected in order to minimize the steric repulsions between the phenyl rings. This twist is probably due to steric interactions between the Cp′ ring protons and the phenyl rings.

In addition, in some early−late heterobimetallics where metal−metal bonding is implicated, recent theoretical studies[7] have established that core distorsions from planarity allow for a closer approach of the metal centers, rendering the energetically preferred geometry. In the present complex the central TiS_2Pd core is also slightly puckered, showing an angle of 19.34° between the S(1)−Pd−S(2) and S(1)−Ti−S(2) planes. This puckering is similar to those observed in the binuclear Ti(IV)−Cu(I) complexes $[Cp_2Ti(\mu\text{-}SEt)_2CuL]$ (L = PPh_3, 13.2°; L = PCy_3, 17.92°][6e] or $[Cp_2Ti(\mu\text{-}(SMe)_2Cu(NCMe)_2]PF_6$ [11°][6d] and is in contrast with the TiS_2M planar cores found in $[Cp_2Ti\{\mu\text{-}(S(CH_2)_nPPh_2\}_2M]BF_4$ (n = 2, M = Cu;[6g] n = 3, M = Rh[8b]], $[Cp_2Ti(\mu\text{-}\{S(CH_2)_3PPh_2\}_2Ni]$,[6f] $[\{Cp^2Ti(\mu\text{-}SMe)_2\}_2Ni]$,[6c] or $[Cp_2Ti(\mu\text{-}SMe)_2Mo(CO)_4]$.[17] Both the acute angles at the sulfur atoms and the "butterfly" shape of the core seem to suggest that the acidic Ti atom accepts electron density from the Pd center. The Ti···Pd distance is found to be 3.140 (3) Å. Although this distance is similar or even less than the Ti···M distances seen in related Ti−late-metal thiolate-bridged heterobimetallics, it is clearly larger than the sum of the covalent radii (2.63 Å), suggesting that in the present complex the metal−metal dative interaction is probably weak.

IR and NMR Spectra. All complexes show two absorptions in the 801−775-cm^{-1} region corresponding to the X-sensitive mode of vibration of the C_6F_5 groups as expected for complexes of this type with two C_6F_5 groups mutually *cis*.[10,11,18]

The ^1H and ^{19}F NMR spectra reveal that, as is usual for other heterobimetallics derived from d^0 bent metallocene thiolates,[6de,8,16ab,19] these derivatives are stereochemically nonrigid in solution. According to the proposed formulas (assuming free rotation of thiolate R groups about the C−S bond) the complexes have a formal symmetry plane passing through the metal atoms which makes the C_6F_5 groups and the R groups equivalent. So, one should expect to observe, in the ^{19}F NMR spectra, a single set (for **1**, **2** and **5**, **6**; M−C_6F_5, SPh) or two different sets (for **3**, **4** and **7**, **8** M−C_6F_5, SC_6F_5) of signals due to the presence of one or two chemically different C_6F_5 ligands, respectively. Similarly, the ^1H NMR spectra should display signals corresponding to the presence of two nonequivalent Cp (for **1**−**4**) or Cp′ (for **5**−**8**) due to the *syn* conformation of the complexes.

The room temperature spectra of complex $[Cp_2Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ (**2**) are consistent with a relatively rigid molecular geometry in solution. Thus, the ^1H NMR spectrum of **2** shows two singlet resonances of equal intensity at δ = 6.19 and 5.47 ppm assigned to the two inequivalent Cp groups and two multiplets at δ = 7.57 and 7.31 ppm (ratio 2:3) assigned to the protons of the benzenethiolate-bridging ligands. The ^{19}F NMR spectrum exhibits a set of five signals of equal intensity, thus confirming that both C_6F_5 groups are equivalent but the five fluorine nuclei on each C_6F_5 are inequivalent. This pattern is in keeping with the structure found for complex **5** and indicates that rotation of C_6F_5 groups about their Pt−C bonds is restricted.

By contrast, at room temperature, the ^1H spectra of the heterobimetallic titanocenethiolate bridged analogues $[Cp_2Ti(\mu\text{-}SR)_2M(C_6F_5)_2]$ (M = Pd, R = Ph (**1**); M = Pd, R = C_6F_5 (**3**), and M = Pt, R = C_6F_5 (**4**)) only exhibit a singlet resonance in the cyclopentadienyl region (see Experimental Section). The broadness of this signal for complexes **1** (6.2 ppm) and **4** (6.02 ppm) led us to examine their spectra at low temperature. In both cases when the system is cooled (−80° for **1** and −50° for **4**), this signal splits into two sharp resonances (δ = 6.55 and 5.80 ppm for **1**, and δ = 6.34 and 5.32 ppm for **4**). As expected, the ^{19}F NMR spectra are also temperature dependent.

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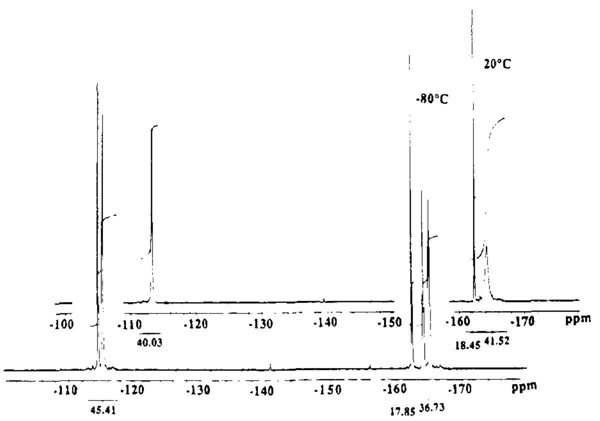

Figure 2. ^{19}F NMR spectra [$(CD_3)_2CO$] of complex [$(\eta^5-C_5H_5)_2Ti(\mu-SPh)_2Pd(C_6F_5)_2$] (**1**) at different temperatures.

Thus, at room temperature the ^{19}F NMR spectrum of Ti−Pd complex **1** (R = Ph) in $(CD_3)_2CO$ shows just three signals (−113.4 ppm, d, F_o; −162.4 ppm, t, F_p, and −164.4 ppm, s, br, F_m) (see Figure 2), corresponding to a single set of C_6F_5. This pattern suggests a time-averaged plane of symmetry at room temperature which renders the two halves of each C_6F_5 equivalent. As can be seen (Figure 2), when the temperature is lowered (−80 °C), the spectrum shows inequivalence of the two ortho fluorines and the two meta fluorine atoms. Analogously, the two sets of three signals observed in the ^{19}F NMR spectrum of Ti−Pt complex **4** (R = C_6F_5) at room temperature (corresponding to C_6F_5 and SC_6F_5 ligands) are clearly resolved at low temperature (−50 °C) into two sets of five signals each (see Experimental Section). This is consistent with the observation at low temperature of two inequivalent ortho and meta fluorine atoms (*endo* and *exo*) on either C_6F_5 (bound to Pt) and μ-SC_6F_5 ligands. Averaging of these environments (*exo* and *endo* F atoms and the Cp environments in the ^{1}H NMR spectra as well) at room temperature may occur through a mechanism involving a simultaneous piramidal inversion on the sulfur atoms. This mechanism has been previously proposed for other sulfur-bridged bimetallic complexes.[6d,20] We noted that the alternative mechanism involving sequential inversion at one sulfur at a time would require the presence of an intermediate *anti* isomer; however, no evidence for this has been observed in the ^{1}H and ^{19}F spectra. The reason for the fact that the *syn* conformation seems to be thermodynamically favored is not clear; however, it is noteworthy that similar thermodynamic favoring of the *syn* conformation in other thiolato-bridged bimetallics has been observed.[6d,e,8b,17,19a,21]

The titanium−platinum and −palladium complexes **5**−**8** derived from [$(\eta^5-C_5H_4SiMe_3)_2Ti(SR)_2$] (R = Ph, C_6F_5) complexes exhibit a similar behavior. Thus, the room temperature ^{19}F NMR spectra of pentafluorobenzenethiolate derivatives **7** (M = Pd) and **8** (M = Pt) only show two sets of three signals (ratio 2:1:2) assigned to C_6F_5 and SC_6F_5 ligands, thus indicating that probably a very fast inversion on the sulfur atoms at room temperature equalizes the *endo* and *exo* fluorine atoms of each C_6F_5 group. As expected, averaging of the Cp′ environments is also observed in their ^{1}H NMR spectra. Thus, for both complexes **7** and **8** magnetic equivalence of the $C_5H_4SiMe_3$ rings on Ti is implied by the observation of a single sharp $SiMe_3$ resonance (at 0.34 ppm for **7** and at 0.33 ppm for **8**) and only two singlets of equal intensities at 6.5 and 6.1 ppm for **7** and at 6.31 and 5.88 ppm for **8** assigned to the hydrogens on the $C_5H_4SiMe_3$ rings. For complex **8** the ^{1}H and ^{19}F spectra were also registered at low temperature. At −50 °C the ^{1}H NMR spectrum exhibits two sharp $SiMe_3$ singlets of equal intensity at 0.39 and 0.83 ppm and eight peaks (6.70, 6.60, 6.55, 6.50, 6.01, 5.65, 5.50, and 4.95 ppm) in the cyclopentadienyl region, suggesting that the two $C_5H_4SiMe_3$ groups are inequivalent. However, at −50 °C the ^{19}F NMR spectrum of **8** resolved into four different sets of signals associated with the presence of two inequivalent terminal C_6F_5 groups [$Pt(C_6F_5)_2$] and two inequivalent bridging SC_6F_5 ligands (see Experimental Section). This pattern indicates the lack of a symmetry plane passing through Ti and Pt atoms at low temperature and suggests that in this case a second temperature dependent process is also frozen at low temperature which is obviously related to hindrance of the rotation of the bulky C_6F_5 groups around the C_6F_5−S bonds.

The benzenethiolate-bridged heterobimetallic derivatives seem to be relatively more rigid in solution; at room temperature the ^{19}F NMR spectra of complexes **5** (M = Pd) and **6** (M = Pt) with R = Ph show the expected set of five signals of equal intensity (two ortho, one para, and two meta), confirming that both C_6F_5 groups are equivalent but the five fluorine nuclei on each C_6F_5 are inequivalent. The room temperature ^{1}H NMR spectra of complex **6** (see Figure 3) exhibit resonances at δ = 7.60−7.31 ppm, assignable to the phenyl protons, four broad peaks at δ = 6.42, 6.30, 5.74, and 5.12 ppm, assignable to the four hydrogen atoms of the two cyclopentadienyl rings, and two sharp singlets at δ = 0.42 and 0.30 ppm, due to the nonequivalent $SiMe_3$ groups. When the temperature is raised to +50 °C, the resonances due to the cyclopentadienyl protons become sharper and only a single $SiMe_3$ broad resonance centered at 0.45 ppm is observed. However, when the solution was cooled, the four broad peaks due to the hydrogen atoms of the cyclopentadienyl rings broadened, coalesced at ca. −30 °C, and finally resolved into eight resonances with chemical shifts at 6.97, 6.70, 6.30, 6.20, 5.82, 5.65, 5.20, and 4.65 ppm, respectively.

Similarly, at low temperature (−50 °C), the ^{1}H NMR spectrum of complex **5** exhibits eight peaks (see Experimental Section) in the cyclopentadienyl region and two sharp $SiMe_3$ singlets at 0.38 and 0.24 ppm, indicative that the two $C_5H_4SiMe_3$ groups are inequivalent. Warming to +20 °C produces three broad resonances in the Cp region and only a broad signal centered at 0.31 for the $SiMe_3$ groups.

Experimental Section

cis-[$M(C_6F_5)_2(THF)_2$] (M = Pt, Pd),[9] [$Cp_2Ti(SR)_2$] (R = Ph,[14] SC_6F_5[23]), and [$(Cp')_2Ti(SR)_2$] (R = Ph, C_6F_5)[12] were prepared by published procedures. All reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen prior to use.

IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer, using Nujol mulls between polyethylene sheets. ^{1}H and ^{19}F NMR spectra were recorded on Brucker ARX 300 and Varian Unity 300 spectrometers. Chemical shifts are reported in parts per million relative to external standards (TMS for ^{1}H and $CFCl_3$ for ^{19}F). Elemental analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Mass spectra were recorded on a V. G. Autospec spectrometer.

[$Cp_2Ti(\mu-SPh)_2Pd(C_6F_5)_2$] (1). To a burgundy solution of [$Cp_2Ti(SPh)_2$] (0.102 g, 0.257 mmol) in CH_2Cl_2 (15 cm^3) was added *cis*-[$Pd(C_6F_5)_2(THF)_2$] (0.150 g, 0.257 mmol), and the mixture was stirred at room temperature for 15 min. Concentration of the resulting orange-red solution (*ca.* 5 cm^3) produced complex **1** as an orange solid, yield 75%. Anal. Found (calcd): 48.20 (48.79); H, 2.46 (2.41); S, 7.55

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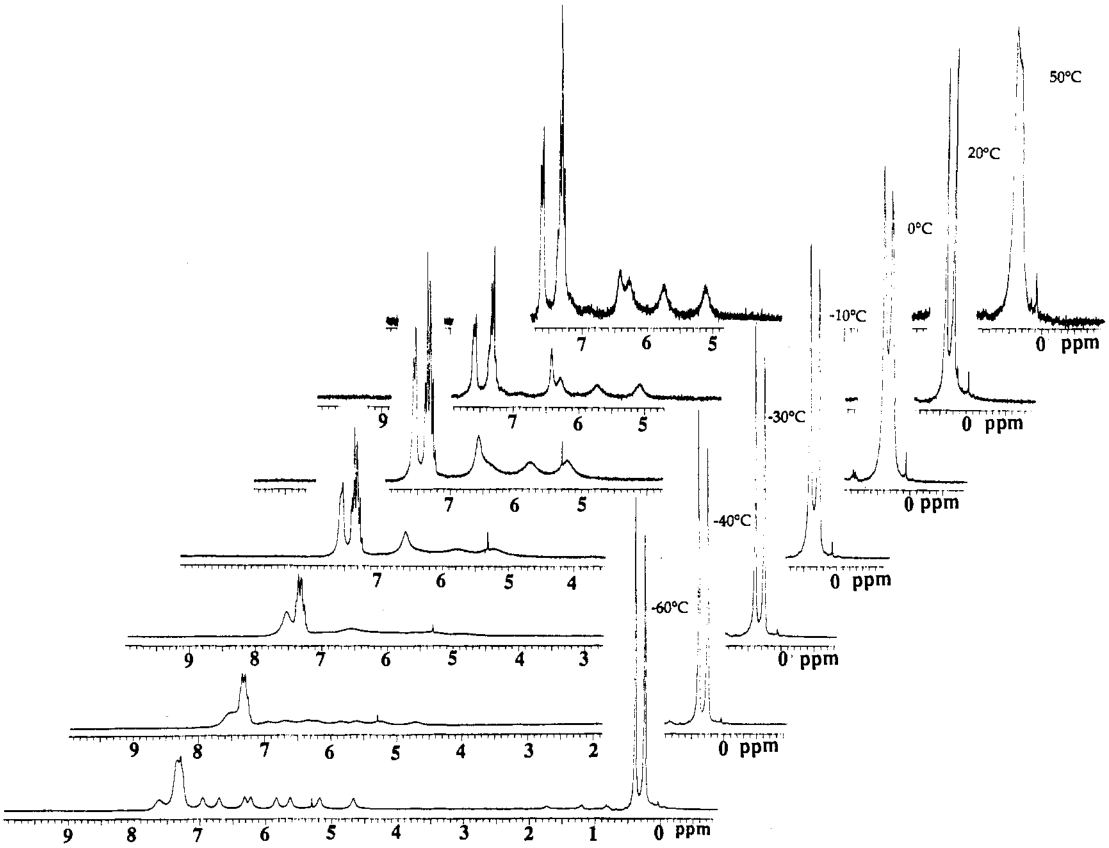

Figure 3. ^{1}H NMR spectra ($CDCl_3$) of complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ (**6**) at different temperatures.

(7.66). EI-MS: molecular peak not observed, $m/z = 669$ $[M - C_6F_5]^+$ (61%); $m/z = 502$ $[M - 2\ C_6F_5]^+$ (87%). IR (cm^{-1}): $\nu(C_6F_5)$X-sens 784 (s), 775 (s). ^{1}H NMR (CD_3COCD_3): at 20 °C, δ 7.67 (d, 4 H, H_{ortho}, Ph), 7.44–7.3 (m, 6 H, H_{meta} and H_{para}, Ph), 6.2 (s, very broad, 10 H, Cp); at −80 °C, δ 7.95–7.35 (m, broad, Ph), 6.55 (s, Cp), 5.80 (s, Cp). ^{19}F NMR (CD_3COCD_3): at 20 °C, δ −113.4 (d, F_{ortho}), −162.4 (t, F_{para}), −164.4 (s, br, F_{meta}); at −80 °C, δ −114.6 (d), −115.3 (d) (F_{ortho}), −162.4 (t, F_{para}), −164.1 (m), −165.0 (m) (F_{meta}).

$[Cp_2Ti(\mu\text{-}SPh)_2Pt(C_6F_5)_2]$ (2). The reaction was performed as described for complex **1** starting from *cis*-$[Pt(C_6F_5)_2(THF)_2]$ (0.093 g, 0.138 mmol) and $[Cp_2Ti(SPh)_2]$ (0.055 g, 0.138 mmol). In this case, **2** was precipitated, as a red solid, by adding *n*-hexane (2 cm^3) and cooling at −30 °C overnight, yield 71%. Under these conditions, **2** crystallizes with CH_2Cl_2 (observed by ^{1}H NMR) as **2**·0.5 CH_2Cl_2. Anal. Found (calcd): C, 42.57 (42.80); H, 2.24 (2.29); S, 6.24 (6.62). EI-MS: molecular peak not observed, $m/z = 758$ $[M - C_6F_5]^+$ (14%); $m/z = 591$ $[M - 2\ C_6F_5]$ (48%). IR (cm^{-1}): $\nu(C_6F_5)$X-sens 799 (s), 789 (s). ^{1}H NMR ($CDCl_3$): δ 7.57 (m, 4 H, H_{ortho}, Ph), 7.31 (m, 6 H, H_{meta} and H_{para}, Ph), 6.19 (s, 5 H, Cp), 5.47 (s, 5 H, Cp). ^{19}F NMR ($CDCl_3$): δ −118.0 (m, $^3J_{Pt-F_o}$= 243 Hz), −118.6 (d, $^3J_{Pt-F_o}$= 412 Hz) (F_{ortho}), −162.5 (t, F_{para}), −163.9 (m), −165.1 (m) (F_{meta}).

$[Cp_2Ti(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ (3). To a garnet solution of $[Cp_2Ti(SC_6F_5)_2]$ (0.079 g, 0.137 mmol) in 10 cm^3 of toluene was added *cis*-$[Pd(C_6F_5)_2(THF)_2]$ (0.080 g, 0.137 mmol) giving immediately an orange solution. After a few minutes of stirring, an orange solid precipitates. The mixture was stirred for 10 min and then cooled to −30 °C. The orange solid **3** was isolated in 70% yield. Anal. Found (calcd): 39.96 (40.16); H, 1.60 (0.99); S, 5.99 (6.31). EI-MS: molecular peak not observed, $m/z = 483$ $[TiCp_2(SC_6F_5)Pd]^+$ (23%); $m/z = 377$ $[TiCp_2(SC_6F_5)]^+$ (56%). IR (cm^{-1}): $\nu(C_6F_5)$X-sens 786 (s), 775 (sh). ^{1}H NMR ($CDCl_3$): at 20 °C, δ 6.16 (Cp). ^{19}F NMR ($CDCl_3$): at 20 °C, δ −116.5 (s, F_{ortho}, C_6F_5), −129.6 (s, F_{ortho}, SC_6F_5), −150.9 (td, F_{para}, SC_6F_5), −159.4 (s, F_{meta}, SC_6F_5), −160.2 (td, F_{para}, C_6F_5), −163.0 (m, F_{meta}, C_6F_5).

$[Cp_2Ti(\mu\text{-}SC_6F_5)_2Pt(C_6F_5)_2]$ (4). This complex was prepared in a similar way to **2** by using the appropiate Ti metalloligand, $[Cp_2Ti(SC_6F_5)_2]$ (0.128 g, 0.222 mmol) and 1 equiv of *cis*-$[Pt(C_6F_5)_2(THF)_2]$ (0.150 g, 0.222 mmol). **4** was isolated as red-garnet crystals in 40% yield. Anal. Found (calcd): C, 36.75 (36.94); H, 1.30 (0.91); S, 5.46 (5.80). EI-MS: molecular peak not observed, $m/z = 377$ $[Cp_2Ti(SC_6F_5)]^+$ (23%). IR (cm^{-1}): $\nu(C_6F_5)$X-sens 800 (vs), 792 (vs). ^{1}H NMR ($CDCl_3$): at 20 °C, δ 6.02 (s, br, Cp); at −50 °C, δ 6.34 (s, Cp), 5.32 (s, Cp). ^{19}F NMR ($CDCl_3$): at 20 °C, δ −119.0 (br, F_{ortho}, C_6F_5), −130.1 (s, F_{ortho}, SC_6F_5), −150.4 (t, F_{para}, SC_6F_5), −159.5 (br, F_{meta}, SC_6F_5), −160.7 (t, F_{para}, C_6F_5), −163.5 (br, F_{meta}, C_6F_5); at −50 °C, δ −118.0 (d, $^3J_{Pt-F_o}$ = 440 Hz), −121.4 (m, $^3J_{Pt-F_o}$ = 367) [F_{ortho}, C_6F_5], −130.0 (d), −130.7 (m) [F_{ortho}, SC_6F_5], −149.8 (t, F_{para}, SC_6F_5), −157.2 (m), −160.0 (m) [F_{meta}, SC_6F_5], −160.4 (t, F_{para}, C_6F_5), −162.3 (m), −163.7 (m) [F_{meta}, C_6F_5].

$[Cp'_2Ti(\mu\text{-}SPh)_2M(C_6F_5)_2]$, M = Pd (5), Pt (6). $[(Cp')_2Ti(SPh)_2]$ (0.100 g, 0.185 mmol) and *cis*-$[Pd(C_6F_5)_2(THF)_2]$ (0.108 g, 0.185 mmol) (for **5**) or *cis*-$[Pt(C_6F_5)_2(THF)_2]$ (0.124 g, 0.185 mmol) (for **6**) were combined following the procedure described for the preparation of complexes **2** and **4**. Complex **5** was isolated as red microcrystalline solid in 48% yield. Complex **6** precipitated as a dark red solid (yield 71%).

Data for **5**: Anal. Found (calcd): C, 48.37 (48.96); H, 3.92 (3.70); S, 6.73 (6.53). EI-MS: molecular peak not observed, $m/z = 813$ $[M - C_6F_5]^+$ (6%), $m/z = 646$ $[M - 2C_6F_5]$ (7%), $m/z = 537$ $[(Cp')_2Ti(SPh)Pd]$ (21%), $m/z = 431$ $[(Cp')_2Ti(SPh)]^+$ (72%), $m/z = 322$ $[(Cp')_2Ti]$ (100%). IR (cm^{-1}): $\nu(C_6F_5)$X-sens 782 (vs), 774 (vs). ^{1}H NMR ($CDCl_3$): at 20 °C, δ 7.55–7.26 (m, 10 H, Ph), 6.55 (s, br), 5.77 (s, br), 5.23 (s, br) (8 H, C_5H_4), 0.31 (s, br, 18 H, $SiMe_3$); at −50 °C, δ 7.6–7.3 (m, br, Ph), 6.97 (s), 6.71 (s), 6.33 (s), 6.24 (s), 5.85 (s), 5.64 (s), 5.18 (s), 4.67 (s) (8 H, C_5H_4), 0.38 (s, 9 H, $SiMe_3$), 0.24 (s, 9 H, $SiMe_3$). ^{19}F NMR ($CDCl_3$): at 20 °C, δ −115.7 (s), −115.4 (s) (F_{ortho}), −161.2 (t, F_{para}), −163.1 (s), −164.2 (s) (F_{meta}).

Data for **6**: Anal. Found (calcd): C, 44.57 (44.90); H, 3.45 (3.39); S, 5.59 (5.99). EI-MS: molecular peak not observed, $m/z = 902$ $[M - C_6F_5]^+$ (7%), $m/z = 735$ $[M - 2C_6F_5]$ (6%), $m/z = 626$ $[(Cp')_2Ti(SPh)Pt]$ (6%), $m/z = 431$ $[(Cp')_2Ti(SPh)]$ (95%), $m/z = 322$ $[(Cp')_2Ti]$ (100%). IR (cm^{-1}): $\nu(C_6F_5)$X-sens 797 (vs), 790 (vs). ^{1}H NMR ($CDCl_3$): at 20 °C, δ 7.6–7.31 (m, 10 H), 6.42, 6.3, 5.74, 5.12 (broad peaks, 8 H, C_5H_4), 0.42 (s), 0.30 (s) (18 H, $SiMe_3$); at −50 °C δ 7.7–7.3 (m, 10 H, Ph), 6.97 (s), 6.7 (s), 6.3 (s), 6.2 (s), 5.82 (s), 5.65 (s), 5.2, 4.65 (8 H, C_5H_4), 0.39 (s, 9 H, $SiMe_3$), 0.25 (s, 9 H, $SiMe_3$). ^{19}F

Table 2. Crystallographic Data for Complex **5**

formula	$PdTiS_2Si_2F_{10}C_{40}H_{36}$	Z	4
mol wt	981.3	V, Å^3	4142 (1)
space group	$P2_1/c$ (No. 14)	D_{calcd}, g cm^{-3}	1.57
a, Å	10.237 (2)	temp, K	295
b, Å	14.635 (3)	μ(Mo Kα), cm^{-1}	8.5
c, Å	27.651 (6)	R^a	0.056
β, (deg)	90.83 (2)	$R_w{}^b$	0.067

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

NMR ($CDCl_3$): at 20 °C, δ −117.6 (s br, $^3J_{Pt-F_o} = 350$ Hz), −118.3 (d, $^3J_{Pt-F_o} = 415$ Hz) (F_{ortho}), −162.4 (t, F_{para}), −163.8 (m), −164.7 (m) (F_{meta}).

[$Cp'_2Ti(\mu$-$SC_6F_5)_2M(C_6F_5)_2$], M = Pd (7), Pt (8). Synthesis of **7** and **8** was performed as described for **3** with the use of the appropiate Ti metalloligand, [$(Cp')_2Ti(SC_6F_5)_2$] (0.100 g, 0.139 mmol) and 1 equiv of *cis*-[$Pd(C_6F_5)_2(THF)_2$] (0.081 g, 0.139 mmol) (for **7**) or *cis*-[$Pt(C_6F_5)_2(THF)_2$] (0.094 g, 0.139 mmol) (for **8**). Complex **7** separated as an orange solid in 60% yield and **8** as a red-garnet solid in 53% yield.

Data for **7**: Anal. Found (calcd): C, 40.78 (41.37); H, 2.72 (2.26); S, 5.24 (5.52). EI-MS: molecular peak not observed, $m/z = 521$ [$(Cp')_2Ti(SC_6F_5)$] (12%), $m/z = 488$ [$(Cp')_2Ti(C_6F_5)$] (33%), $m/z = 322$ [$(Cp')_2Ti$] (100%). IR (cm^{-1}): $\nu(C_6F_5)$X-sens 787 (s), 776 (s). ^{1}H NMR ($CDCl_3$): at 20 °C, δ 6.5 (s, 4 H), 6.1 (s, 4 H) (C_5H_4), 0.34 (s, 18 H, $SiMe_3$). ^{19}F NMR ($CDCl_3$): at 20 °C, δ −116.5 (s, F_{ortho}, C_6F_5), −128.8 (s, F_{ortho}, SC_6F_5), −151.0 (m, F_{para}, SC_6F_5), −159.6 (s, br, F_{meta}, SC_6F_5), −160.3 (m, F_{para}, C_6F_5), −163.1 (s, br, F_{meta}, C_6F_5).

Data for **8**: Anal. Found (calcd): C, 37.88 (38.44); H, 2.57 (2.10); S, 5.12 (5.13). EI-MS: molecular peak not observed, $m/z = 521$ [$(Cp')_2Ti(SC_6F_5)$] (23%); $m/z = 322$ [$(Cp')_2Ti$] (100%). IR (cm^{-1}): $\nu(C_6F_5)$X-sens 801 (vs), 790 (s). ^{1}H NMR ($CDCl_3$): at 20 °C, δ 6.31 (s, br, 4 H), 5.88 (s, br, 4 H) (C_5H_4), 0.33 (s, 18 H, $SiMe_3$); at −50 °C, δ 6.70 (s, 1H), 6.60, 6.55, 6.50 (three peaks overlapping 3 H), 6.01 (s, 1 H), 5.65 (s, 1 H), 5.50 (s, 1 H), 4.95 (s, 1 H), 0.39 (s, 9 H, $SiMe_3$), 0.83 (s, 9 H, $SiMe_3$). ^{19}F NMR ($CDCl_3$): at 20 °C, δ −119.5 (s, br, Pt satellites are observed but they are not well resolved, F_{ortho}, C_6F_5), −129.1 (s, F_{ortho}, SC_6F_5), −150.4 (t, F_{para}, SC_6F_5), −156.7 (s, br, F_{meta}, SC_6F_5), −160.9 (t, F_{para}, C_6F_5), −163.7 (s, br, F_{meta}, C_6F_5); at −50 °C, −118.0 (d, $^3J_{Pt-F_o} = 465$ Hz), −118.3 (d, $^3J_{Pt-F_o} = 419$ Hz), −120.6 (d, $^3J_{Pt-F_o} \approx 350$ Hz), −122.0 (s, $^3J_{Pt-F_o} \approx 355$ Hz) (4 F_{ortho}, C_6F_5), −128.6 (d, 1 F), −129.4 (s, 1 F), −129.9 (d, 2 F) (F_{ortho}, SC_6F_5), −148.8 (t, br, 1 F), −150.7 (t, br, 1 F) (F_{para}, SC_6F_5), −157.0 (s, 1 F), −157.3 (s, 1 F) (F_{meta}, SC_6F_5), −160.2 (m, 3 F, 1 F_{meta}, SC_6F_5; 2 F_{para}, C_6F_5), −160.7 (1 F, F_{meta}, SC_6F_5), −162.5 (m), −163.4 (m), −164.0 (m) (4 F, F_{meta}, C_6F_5).

X-ray Structure Determinations. Suitable crystals for the X-Ray diffraction study were obtained by the slow diffusion of *n*-hexane into a dichloromethane solution of complex **5** at −40 °C. The crystal data are summarized in Table 2 and fractional atomic coordinates are given in Table 3. A pale reddish crystal of prismatic shape and dimensions 0.10 × 0.10 × 0.08 mm was mounted on a Enraf-Nonius CAD4 diffractometer with a graphite-monochromated Mo Kα radiation source ($\lambda = 0.710\,69$ Å).

The cell dimensions were refined by least-squares fitting of the θ values of 25 accurate centered reflections within a 2θ range of 5°−22°. Data were collected at 295 K using the $\omega - 2\theta$ scan technique to a maximum $2\theta = 56°$, from (−13,0,0) to (13,19,36) to yield 10020 unique reflections, among them 2665 were considered observed, having $I > 3\sigma(I)$. The stability of the crystal was monitored every 100 reflections using three standard reflections; no significant decay of their intensities was observed.

The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Pd, Ti, Si, and S were taken from the *International Tables for X-Ray Crystallography*.[24]

The structure was solved by Patterson and Fourier methods. Since the crystal was very small and almost cubic in shape, and the calculated linear absorption coefficient was relatively small, no absorption correction was applied.

Table 3. Atomic Coordinates for Complex **5**

atom	*X/A*	*Y/B*	*Z/C*
Pd	0.454 04(11)	0.242 96(8)	0.890 09(4)
Ti	0.536 61(27)	0.172 60(18)	0.787 68(10)
S1	0.666 99(39)	0.221 84(25)	0.858 12(15)
S2	0.328 07(38)	0.162 90(26)	0.830 70(15)
Si1	0.340 36(45)	0.226 05(32)	0.666 16(17)
Si2	0.857 21(47)	0.096 21(35)	0.722 10(18)
F1	0.590 21(100)	0.197 89(64)	0.993 13(34)
F2	0.719 54(98)	0.301 72(80)	1.055 63(36)
F3	0.743 38(108)	0.482 51(76)	1.039 88(37)
F4	0.641 17(118)	0.557 50(72)	0.958 21(41)
F5	0.509 70(106)	0.454 37(67)	0.894 28(38)
F6	0.317 88(106)	0.187 16(85)	0.991 25(40)
F7	0.097 03(134)	0.242 20(125)	1.030 04(48)
F8	−0.062 75(131)	0.361 65(122)	0.982 20(60)
F9	0.008 23(110)	0.424 98(96)	0.895 07(59)
F10	0.231 80(105)	0.374 85(75)	0.855 99(41)
C1	0.543 13(140)	0.320 92(104)	0.941 40(53)
C2	0.602 67(158)	0.287 51(114)	0.982 70(58)
C3	0.666 75(149)	0.338 20(143)	1.016 24(57)
C4	0.678 51(174)	0.431 19(126)	1.007 63(63)
C5	0.630 09(184)	0.467 56(124)	0.967 22(66)
C6	0.559 60(151)	0.414 79(120)	0.934 66(65)
C7	0.284 36(157)	0.276 44(120)	0.922 83(62)
C8	0.243 89(162)	0.249 08(147)	0.965 70(64)
C9	0.128 79(192)	0.277 00(165)	0.986 48(81)
C10	0.049 81(209)	0.336 65(190)	0.962 32(97)
C11	0.088 17(210)	0.366 66(144)	0.918 98(93)
C12	0.204 76(178)	0.339 30(126)	0.899 91(62)
C13	0.447 29(134)	0.257 38(112)	0.719 00(47)
C14	0.583 80(149)	0.268 42(99)	0.720 77(57)
C15	0.622 17(183)	0.314 19(107)	0.763 66(72)
C16	0.505 16(202)	0.334 00(124)	0.789 19(64)
C17	0.405 91(172)	0.300 16(108)	0.762 38(63)
C18	0.692 83(164)	0.074 58(98)	0.749 59(53)
C19	0.678 16(163)	0.044 10(101)	0.796 24(64)
C20	0.546 68(177)	0.015 24(101)	0.803 23(63)
C21	0.482 85(180)	0.026 18(106)	0.758 80(79)
C22	0.569 10(159)	0.063 96(108)	0.725 56(58)
C25	0.746 75(164)	0.137 89(113)	0.893 21(57)
C26	0.883 12(179)	0.144 13(126)	0.897 56(69)
C27	0.946 05(220)	0.077 39(179)	0.923 57(91)
C28	0.889 31(279)	0.004 80(187)	0.94538(87)
C29	0.758 27(231)	0.001 48(153)	0.940 04(65)
C30	0.683 70(179)	0.068 07(126)	0.914 58(64)
C31	0.280 98(143)	0.056 46(95)	0.855 29(58)
C32	0.202 47(165)	−0.001 25(119)	0.827 61(64)
C33	0.157 90(185)	−0.083 90(128)	0.848 13(89)
C34	0.196 52(204)	−0.107 53(131)	0.891 79(88)
C35	0.273 03(210)	−0.053 43(136)	0.919 11(72)
C36	0.318 13(154)	0.028 67(104)	0.901 36(59)
C231	0.265 51(176)	0.113 42(140)	0.670 70(74)
C232	0.443 61(211)	0.233 05(185)	0.613 07(65)
C233	0.206 88(179)	0.311 58(141)	0.663 24(79)
C241	0.945 21(189)	−0.014 76(120)	0.729 36(69)
C242	0.844 00(182)	0.124 51(143)	0.658 23(72)
C243	0.945 08(195)	0.184 38(149)	0.757 24(76)

The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by molecular geometry. A final refinement was undertaken with anisotropic thermal parameters for the non-hydrogen atoms.

Since no trend in ΔF vs F_o or sin θ/λ was observed, no special weighting scheme has been applied. Final difference synthesis shows no significant electron density; the maximum value corresponds to a peak of 5.2 e Å^{-3} near the palladium atom (0.3 Å) with no chemical relevance. Most of the calculations were carried out with the X-Ray 80 system.[25]

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Supporting Information Available: Tables of general crystallographic data, all atomic coordinates, bond lengths and angles, and anisotropic displacement parameters (10 pages). Ordering information is given on any current masthead page.

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