Methyl Levamisolium Triflate as a Precursor to a Chiral Bifunctional N-Heterocyclic Carbene-Thiolate Ligand: Palladium(II) Complexes†

Javier A. Cabeza,* Ignacio del Río, M. Gabriela Sánchez-Vega, and Marta Suárez

Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica "Enrique Moles", Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain

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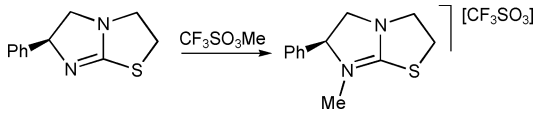
Summary: Cationic palladium(II) complexes containing the chiral N-heterocyclic carbene (NHC) ligand 1-ethylenethiolate-3-methyl-4-(R)-phenylimidazoline-2-ylidene have been prepared in one-pot reactions that involve the oxidative addition of the C−S bond of methyl levamisolium to [Pd(dba)$_2$] (dba = dibenzylidene acetone). These reactions represent an easy entry into complexes having chiral NHC ligands.

Introduction

In the last decade, N-heterocyclic carbenes (NHCs) have attracted increasing attention as ancillary ligands[1] because many of their metal complexes, particularly those of metals belonging to groups 8−11 of the periodic table, have been revealed as excellent homogeneous catalysts for processes that are very useful in organic synthesis, most notably C−C bond forming reactions and olefin metathesis.[2] Although a few metal complexes containing chiral NHC ligands have been recently identified as useful catalysts for asymmetric reactions,[2f,3] the number of such complexes is still small,[3,4] probably because the synthesis of chiral NHC ligands in enantiomerically pure form is not a simple task, particularly if the stereogenic atom is in the same ring as the carbene carbon atom.

Scheme 1



We now report that, in the presence of appropriate ancillary ligands, reactions of [Pd(dba)$_2$] (dba = dibenzylidene acetone) with methyl levamisolium triflate, a methylated derivative of levamisole, 2,3,5,6-tetrahydro-6-(*R*)-phenylimidazo[2,1-*b*]thiazole, lead, in one-pot processes, to cationic palladium(II) derivatives that contain the chiral ligand 1-ethylenethiolate-3-methyl-4-(*R*)-phenylimidazoline-2-ylidene. Therefore, this contribution describes an easy entry into complexes having a chiral bifunctional NHC-thiolate ligand.

Levamisole hydrochloride is an inexpensive, commercially available, enantiomerically pure reagent. Levamisole and its hydrochloride have been used as drugs with anthelmintic[5] and anticancer[6] properties.

Results and Discussion

Methyl levamisolium triflate was made in quantitative yield treating levamisole with methyl triflate (Scheme 1). Levamisole was conveniently prepared by deprotonation of commercial levamisole hydrochloride with potassium hydroxide.

The reaction of [Pd(dba)$_2$] with 1 equiv of methyl levamisolium triflate (dichloromethane, room temperature, 18 h) led to a dark red solution from which no pure product could be isolated. However, the addition of ligands to the reaction mixture allowed the isolation of compounds **1**−**4** (Scheme 2).

The binuclear derivative [Pd$_2$(S−C)$_2$(PPh$_3$)$_2$](CF$_3$SO$_3$)$_2$ (**1**), S−C = 1-ethylenethiolate-3-methyl-4-(*R*)-phenylimidazoline-2-ylidene, was best prepared by allowing to react an equimolar mixture of [Pd(dba)$_2$], methyl levamisolium triflate, and triphenylphosphine. The crystal structure of the tetrafluoroborate salt [Pd$_2$(S−C)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ (**1′**), prepared by metathesis of **1** with Na[BF$_4$], was determined by X-ray diffraction methods. The compound crystallizes in the chiral space group *P*1, with two independent (but essentially identical) binuclear dications and four tetrafluoroborate anions in the unit cell. Figure 1 shows the structure of one of these dications. Its most interesting feature is the presence of a 1-ethylenethiolate-3-methyl-4-(*R*)-phenyl-

† Dedicated to Professor José A. Abad, for his important contributions to the organometallic chemistry of palladium, regretting his untimely retirement.

* Corresponding author. E-mail: jac@fq.uniovi.es. Fax: int + 34-985103446.

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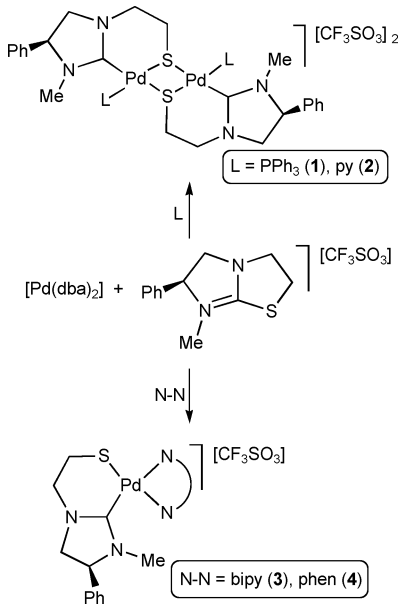
Scheme 2



imidazoline-2-ylidene ligand attached to each palladium atom through the carbene carbon atom, while the thiolate sulfur atom bridges the metal atoms. A triphenylphosphine ligand completes the square planar coordination of each metal atom. A noncrystallographic 2-fold axis, which is maintained in solution, relates the two halves of the dication (Figure 1, top view). The Pd_2S_2 core is not planar, since both PdS_2 planes form a dihedral angle of 144.7(2)°. The substituents of both sulfur atoms adopt an *endo* arrangement (Figure 1, bottom view). This fact is unusual in thiolate-bridged binuclear complexes.[7]

Therefore, the new chiral NHC-thiolate ligand of compound **1** arises from the oxidative addition of the S−C(sp^2) bond of methyl levamisolium to a zerovalent metal species. Such metal-mediated S−C bond cleavage processes are not unusual;[8] in fact, they are key steps in hydrodesulfurization processes,[9] but they generally require high temperatures. The oxidative addition of the Cl−C bond of 2-chloro-1,3-disubstituted imidazolinium salts has also been used to prepare metal complexes with NHC ligands.[3f]

The use of two or more equivalents of triphenylphosphine in the reaction of [Pd(dba)$_2$] with methyl levamisolium triflate resulted in mixtures of compound **1** with a complex containing two PPh_3 ligands, characterized by having two doublets in its $^{31}P\{^1H\}$ NMR spectrum (δ = 21.3 and 23.5, J = 33 Hz), and probably corresponding to the formula $[Pd(S-C)(PPh_3)_2]CF_3SO_3$ (vide infra). Unfortunately, this complex could not be isolated pure because it slowly releases one phosphine ligand in solution to give compound **1**.

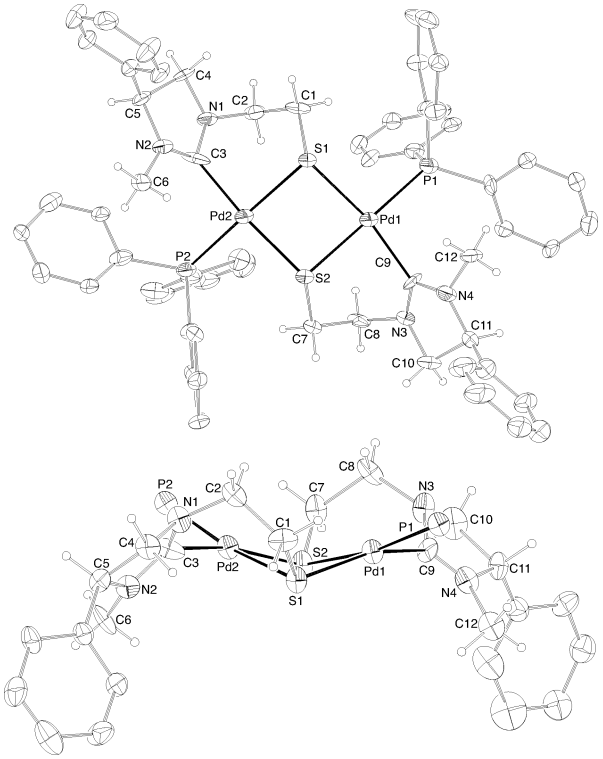


Figure 1. Structure of one of the two independent dications found in the unit cell of **1′**, viewed approximately along the noncrystallographic 2-fold axis (top) and along the S(1)−S(2) vector (bottom). The PPh_3 phenyl groups of the bottom view and all the phenyl hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−P1 2.333(4), Pd1−C9 2.05(1), Pd1−S1 2.381(4), Pd1−S2 2.370(4), Pd2−P2 2.294(4), Pd2−C3 2.04(2), Pd2−S1 2.360(4), Pd2−S2 2.365(4), Pd1−S1−Pd2 90.7(1), Pd1−S2−Pd2 90.9(1).

The addition of pyridine (py), 2,2′-bipyridine (bipy), or 1,10-phenanthroline (phen) to solutions containing [Pd(dba)$_2$] and methyl levamisolium triflate allowed the isolation of the complexes $[Pd_2(S-C)_2(py)_2](CF_3SO_3)_2$ (**2**) and $[Pd(S-C)(N-N)]CF_3SO_3$ (**3**, N−N = bipy; **4**, N−N = phen) (Scheme 1). Curiously, in contrast with the reaction with triphenylphosphine, the binuclear complex **2** was the only product formed in the reaction with pyridine, even using a large excess of the ligand.

While the positive FAB mass spectra of **3** and **4** clearly show their mononuclear nature (signals due to the mass of the corresponding cation are clearly observed), the positive FAB mass spectra of **1** and **2** do not indicate their binuclear character (no signals due to the mass of the corresponding dication or to half of it are observed). Interestingly, the ^1H NMR chemical shifts of one of the protons of the SCH_2 group of the binuclear dications **1** and **2** are shifted 1.0−1.3 ppm toward higher field with respect to those of the mononuclear complexes **3** and **4**, thus representing clear spectroscopic evidence to distinguish bi- from mononuclear derivatives of the S−C ligand. In the $^{13}C\{^1H\}$ NMR spectra of **1**−**4**, the resonance of the carbene carbon atom is observed between 195.8 and 187.2 ppm.

Very few inorganic derivatives of levamisole (lvms) have been reported. They are the complexes $[MCl_2(lvms)_2]$ (M =

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Co, Ni, Cu, Zn),[10] [Pd(aminoacidato)(lvms)]Cl,[11] and [PtCl(en)(lvms)]Cl (en = ethylendiamine),[12] which all have the levamisole ligand coordinated through the sp^2 N atom. A triruthenium derivative that results from the cleavage of the C−S bond of levamisole hydrochloride has also been reported.[13]

Concluding Remarks

We have demonstrated herein that methyl levamisolium triflate, a reagent that is easily prepared from an inexpensive precursor (levamisole hydrochloride), can be used as a source of palladium complexes having chiral bifunctional NHC-thiolate ligands.

It is anticipated that the cleavage of the S−C(sp^2) bond of the reagent, which is the key process of the synthesis of compounds **1**−**4**, may also take place over complexes of other metals in low oxidation states.

Finally, the incorporation of many other substituents (different from methyl, including chiral groups) on the sp^2 N atom of levamisole should be easy. This may lead to a wide variety of levamisolium salts that may be used as precursors to many new complexes having chiral NHC ligands.

Experimental Section

Solvents were dried over sodium diphenyl ketyl (diethyl ether) or calcium hydride (dichloromethane) and were distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk and vacuum line techniques. [Pd(dba)$_2$] was prepared by a literature method,[14] and the remaining reagents were purchased from commercial suppliers. NMR: Bruker DPX-300 (^{1}H ^{31}P) and AV-400 (^{13}C); room temperature; TMS as internal standard for ^{1}H, solvent resonance as internal standard for ^{13}C, and aqueous 85% H_3PO_4 as external standard for ^{31}P. Microanalyses: Perkin-Elmer 2400. MS: VG Autospec double-focusing mass spectrometer operating in the FAB+ mode; ions were produced with a standard Cs^+ gun; 3-nitrobenzyl alcohol (NBA) was used as matrix; data given refer to the most abundant isotopomer. X-ray diffraction: Nonius Kappa-CCD.

Levamisole. A solution of potassium hydroxide in water (10 M) was added dropwise to a suspension of levamisole hydrochloride (1.5 g, 6.23 mmol) in diethyl ether (50 mL) until the complete dissolution of the latter was observed. The two phases were separated. The aqueous phase was washed with diethyl ether (4 × 20 mL), and the combined ethereal extracts were dried with anhydrous sodium sulfate. The solution was concentrated to ca. 10 mL. Hexane (30 mL) was added, and the resulting white solid was filtered, washed with hexane (10 mL), and dried under vacuum (940 mg, 74%). Anal. Calcd for $C_{11}H_{12}N_2S$ (204.29): C, 64.67; H, 5.92; N, 13.71. Found: C, 64.40; H, 5.91; N, 13.72. Specific rotation: $[\alpha]_D$ −105 (*c* 0.01, 298 K, CH_2Cl_2). ^{1}H NMR (300 MHz, 293 K, CD_2Cl_2): δ 7.30−7.27 (m, 5 H), 5.47 (t, J = 8.7 Hz, 1 H), 3.70 (t, J = 8.7 Hz, 1 H), 3.69−3.49 (m, 2 H), 3.39 (m, 1 H), 3.14 (td, J = 8.4 and 6.4 Hz, 1 H), 3.01 (t, J = 8.7 Hz, 1 H). ^{13}C{^{1}H} NMR (100.6 MHz, DEPT, 293 K, CD_2Cl_2): δ 174.7 (C), 143.3 (C), 128.9 (2 CH), 127.6 (CH), 126.9 (2 CH), 77.3 (CH), 58.8 (CH_2), 49.5 (CH_2), 34.5 (CH_2).

Methyl Levamisolium Triflate. Methyl triflate (0.7 mL, 6.19 mmol) was added to a solution of levamisole (1 g, 4.88 mmol) in diethyl ether (50 mL). A white solid precipitated. The suspension was stirred for 2 h. The liquid was decanted, and the solid was washed with diethyl ether (2 × 10 mL) and dried under vacuum (1.60 g, 89%). Anal. Calcd for $C_{13}H_{15}F_3N_2O_3S$ (366.33): C, 46.42; H, 4.50; N, 8.33. Found: C, 46.29; H, 4.58; N, 8.29. Specific rotation: $[\alpha]_D$ −102 (*c* 0.01, 298 K, CH_2Cl_2). ^{1}H NMR (300 MHz, 293 K, CD_2Cl_2): δ 7.50−7.30 (m, 5 H), 5.63 (dd, J = 10.4 and 8.5 Hz, 1 H), 4.47 (t, J = 10.4 Hz, 1 H), 4.21−3.90 (m, 4 H), 3.76 (dd, J = 10.4 and 8.5 Hz, 1 H), 2.92 (s, 3 H). ^{13}C{^{1}H} NMR (100.6 MHz, DEPT, 293 K, CD_2Cl_2): δ 177.2 (C), 135.0 (C), 121.0 (q, J_{C-F} = 320 Hz, C), 130.2 (CH), 129.7 (2 CH), 127.8 (2 CH), 73.2 (CH), 54.9 (CH_2), 48.9 (CH_2), 37.0 (CH_2), 33.7 (CH_3).

$[Pd_2(S-C)_2(PPh_3)_2](CF_3SO_3)_2$ (1). Triphenylphosphine (46 mg, 0.176 mmol) and methyl levamisolium triflate (64 mg, 0.174 mmol) were added to a solution of [Pd(dba)$_2$] (100 mg, 0.174 mmol) in dichloromethane (20 mL). The mixture was stirred at room temperature for 20 h. The color changed from deep purple to orange-yellow. The solvent was removed under reduced pressure. The residue was washed with diethyl ether (2 × 5 mL), and the resulting solid was recrystallized by adding sequentially dichloromethane (3 mL) and diethyl ether (10 mL). The solvent was decanted from an off-white solid, which was washed with diethyl ether (5 mL) and dried under vacuum (80 mg, 62%). Anal. Calcd for $C_{62}H_{60}F_6N_4O_6P_2Pd_2S_4$ (1474.09): C, 50.51; H, 4.10; N, 3.80. Found: C, 50.63; H, 4.18; N, 3.68. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.72−7.53 (m, 13 H), 7.45−7.20 (m, 5 H), 7.00−6.91 (m, 2 H), 4.38−4.20 (m, 2 H), 3.70 (t, br, J = 13.7 Hz, 1 H), 3.52 (m, 1 H), 3.21 (t, J = 9.5 Hz, 1 H), 2.21 (s, 3 H), 1.84 (t, br, J = 13.7 Hz, 1 H), 1.62 (d, J = 13.7 Hz, 1 H). ^{31}P{^{1}H} NMR (121.5 MHz, 293 K, $CDCl_3$): δ 28.0 (s). ^{13}C{^{1}H} NMR (100.6 MHz, DEPT, 293 K, $CDCl_3$): δ 195.8 (d, J_{C-P} = 3.2 Hz, C), 136.1 (C), 134.3−134.0 (m), 133.1 (CH), 130.2−129.7 (m), 129.5−129.1 (m), 128.2−127.5 (m), 127.1 (CH), 121.1 (q, J_{C-F} = 320 Hz, C), 68.1 (CH), 57.1 $(CH)_2$, 54.7 (CH_2), 34.9 (Me), 27.5 (CH_2).

$[Pd_2(S-C)_2(py)_2](CF_3SO_3)_2$ (2). A solution of [Pd(dba)$_2$] (50 mg, 0.087 mmol) and methyl levamisolium triflate (32 mg, 0.087 mmol) in dichloromethane (20 mL) was stirred at room temperature for 18 h. The color changed from deep purple to red-brown. Pyridine (1 drop from a Pasteur pipet) was then added, and the solution was stirred at room temperature for 24 h. The solvent was removed under reduced pressure. The residue was washed with diethyl ether (2 × 5 mL), and the resulting solid was recrystallized by addition of dichloromethane (2 mL) and diethyl ether (8 mL). The solvent was decanted from a brown solid, which was washed with diethyl ether (5 mL) and dried under vacuum (34 mg, 71%). Anal. Calcd for $C_{36}H_{40}F_6N_6O_6Pd_2S_4$ (1107.84): C, 39.03; H, 3.64; N, 7.59. Found: C, 39.18; H, 3.77; N, 7.48. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 9.09 (s, br, 2 H), 7.89 (t, J = 7.6 Hz, 1 H), 7.58 (t, J = 7.6 Hz, 1 H), 7.34−7.15 (m, 5 H), 4.72 (dd, J = 11.2 and 6.3 Hz, 1 H), 4.35 (t, J = 13.3 Hz, 1 H), 4.18 (t, J = 11.2 Hz, 1 H), 3.75 (dd, J = 11.2 and 6.3 Hz, 1 H), 3.25 (d, J = 13.3 Hz, 1 H), 2.49 (s, 3 H), 2.19 (m, br, 1 H), 1.20 (d, J = 13.3 Hz, 1 H). ^{13}C-{^{1}H} NMR (100.6 MHz, DEPT, 293 K, $CDCl_3$): δ 187.3 (C), 153.4 (2 CH), 140.1 (2 CH), 138.2 (C), 129.6 (2 CH), 129.4 (CH), 127.4 (CH), 127.3 (2 CH), 121.1 (q, J_{C-F} = 320 Hz, C), 68.1 (CH), 58.5 (CH_2), 53.0 (CH_2), 35.5 (Me), 25.8 (CH_2).

$[Pd(S-C)(bipy)]CF_3SO_3$ (3). 2,2′-Bipyridine (14 mg, 0.089 mmol) and methyl levamisolium triflate (32 mg, 0.087 mmol) were added to a solution of [Pd(dba)$_2$] (50 mg, 0.087 mmol) in dichloromethane (20 mL), and the mixture was stirred at room temperature for 20 h. The color changed from deep purple to orange. The solvent was removed under reduced pressure. The residue was washed with diethyl ether (2 × 5 mL), and the resulting solid was recrystallized by addition of dichloromethane (2 mL) and diethyl ether (8 mL). The solvent was decanted from an orange solid, which

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was washed with diethyl ether (5 mL) and dried under vacuum (35 mg, 64%). Anal. Calcd for $C_{23}H_{23}F_3N_4O_3PdS_2$ (631.01): C, 43.78; H, 3.67; N, 8.88. Found: C, 44.01; H, 3.73; N, 8.63. FAB-MS: *m*/*z* 482 [M − CF_3SO_3]. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 8.92 (d, J = 5.0 Hz, 1 H), 8.85 (d, J = 5.1 Hz, 1 H), 8.4−7.3 (m, 11 H), 5.59 (dd, J = 10.7 and 8.6 Hz, 1 H), 4.51 (t, J = 10.7 Hz, 1 H), 3.93 (t, br, J = 12.1 Hz, 1 H), 3.70−3.50 (m, 2 H), 3.15 (s, 3 H), 2.72 (t, br, J = 12.1 Hz, 1 H), 2.58 (d, J = 12.1 Hz, 1 H). ^{13}C{^{1}H} NMR (100.6 MHz, DEPT, 293 K, $CDCl_3$): δ 192.5 (C), 156.1 (C), 154.7 (C), 153.5 (CH), 148.9 (CH), 141.1 (CH), 140.7 (CH), 138.7 (C), 129.8 (2 CH), 129.7 (CH), 129.4 (CH), 127.7 (2 CH), 126.9 (CH), 123.6 (CH), 123.3 (CH), 121.1 (q, J_{C-F} = 320 Hz, C), 68.1 (CH), 58.8 (CH_2), 54.9 (CH_2), 35.6 (Me), 26.7 (CH_2).

[Pd(S−C)(phen)]CF_3SO_3 (4). 1,10-Phenanthroline (32 mg, 0.174 mmol) and methyl levamisolium triflate (64 mg, 0.174 mmol) were added to a solution of [Pd(dba)$_2$] (100 mg, 0.174 mmol) in dichloromethane (30 mL), and the mixture was stirred at room temperature for 24 h. The color changed from deep purple to pale orange. The solvent was removed under reduced pressure. The residue was washed with diethyl ether (2 × 5 mL), and the resulting solid was recrystallized by addition of dichloromethane (3 mL) and diethyl ether (10 mL). The solvent was decanted from a greenish-yellow solid, which was washed with diethyl ether (5 mL) and dried under vacuum (75 mg, 66%). Anal. Calcd for $C_{25}H_{23}F_3N_4O_3PdS_2$ (655.02): C, 45.84; H, 3.54; N, 8.55. Found: C, 45.91; H, 3.58; N, 8.42. FAB-MS: *m*/*z* 505 [M − CF_3SO_3]. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 9.38 (dd, J = 5.1 and 1.3 Hz, 1 H), 9.23 (dd, J = 5.1 and 1.3 Hz, 1 H), 8.68 (dd, J = 8.3 and 1.3 Hz, 1 H), 8.65 (dd, J = 8.3, 1.3 Hz, 1 H), 8.35 (dd, J = 8.3 and 5.1 Hz), 8.14−8.05 (m, 2 H), 7.97 (dd, J = 8.3 and 5.1 Hz, 1 H), 7.32−7.48 (m, 5 H), 5.73 (dd, J = 10.5 and 8.3 Hz, 1 H), 4.60 (t, J = 10.5 Hz, 1 H), 4.00 (t, br, J = 12.1 Hz, 1 H), 3.72 (m, 1 H), 3.62 (dd, J = 10.5 and 8.3 Hz, 1 H), 3.22 (s, 3 H), 2.80 (td, J = 12.1 and 3.0 Hz, 1 H), 2.62 (d, J = 12.1 Hz, 1 H). ^{13}C{^{1}H} NMR (100.6 MHz, DEPT, 293 K, $CDCl_3$): δ 191.6 (C), 155.7 (CH), 149.1 (CH), 147.0 (C), 145.9 (C), 1.39.6 (CH), 139.1 (CH), 138.8 (C), 130.7 (C), 130.4 (C), 129.8 (2 CH), 129.3 (CH), 128.7 (CH), 128.2 (CH), 127.8 (2 CH), 127.3 (CH), 125.4 (CH), 121.1 (q, J_{C-F} = 320 Hz, C), 68.1 (CH), 58.9 (CH_2), 55.1 (CH_2), 35.7 (Me), 26.6 (CH_2).

Preparation of Tetrafuoroborate Salts. As all our attempts to obtain X-ray diffraction-quality crystals of compounds **1**−**4** were unsuccessful, we decided to prepare the tetrafluoroborate salts of the cations of **1**−**4**. As they all were prepared similarly, only the synthesis of [Pd_2(S−C)$_2$(PPh_3)$_2$](BF_4)$_2$ (**1′**) is described: A saturated solution of sodium tetrafluoroborate in water (1 mL) was added to a solution of compound **1** (30 mg, 0.020 mmol) in methanol (15 mL). The resulting mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum, and the residue was extracted into dichloromethane (3 × 5 mL). The extract was dried with anhydrous magnesium sulfate, filtered, and evaporated to dryness. The solid residue was washed with diethyl ether (5 mL) and dried under vacuum (18 mg, 67%). Anal. Calcd for $C_{60}H_{60}B_2F_8N_4P_2Pd_2S_2$ (1349.69): C, 53.39; H, 4.48; N, 4.15. Found: C, 53.44; H, 4.52; N, 4.08.

X-ray Structure of [Pd_2(S−C)$_2$(PPh_3)$_2$](BF_4)$_2$ (1′). Very small, low-quality, crystals of **1′** were obtained by diffusion of diethyl ether into a solution of the complex in acetone. Diffraction data were collected on a Nonius Kappa-CCD diffractometer, using graphite-monochromatized Cu Kα radiation. Although various data sets were obtained from different crystals, they all contained very low-intensity reflections. The best data set was used for the structure determination. Despite the low intensity of the reflections, the structure was solved by Patterson interpretation in the chiral space group *P*1, using DIRDIF-96,[15] and the atom connectivity could be inferred. Two independent dicationic binuclear complexes and four tetrafluoroborate anions were found in the asymmetric unit. Isotropic and full matrix anisotropic least-squares refinements against F^2 were carried out using SHELXL-97.[16] All non-H atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. Empirical or semiempirical absorption corrections on the data set resulted in several nonpositive definite thermal ellipsoids when anisotropic refinement was performed; therefore, no absorption correction was carried out. The refinement of this model converged with a high discrepancy index (R = 0.1281) because, due to the low-intensity data set, many essentially "unobserved" reflections were used in the refinement. Therefore, although the reported atom connectivity is correct, the accuracy of the obtained bond distances and angles is low. The molecular plots were made with the PLATON program package.[17] The WINGX program system[18] was used throughout the structure determination. Selected crystallographic data for **1′**: $C_{60}H_{60}B_2F_8N_4P_2Pd_2S_2$, M = 1349.69, triclinic, a = 13.3185(9) Å, b = 13.5907(11) Å, c = 20.5690(19) Å, α = 81.075(4)°, β = 88.287(5)°, γ = 63.849(4)°, U = 3298.5(5) Å^3, T = 200(2) K, space group *P*1, Z = 2, μ(Cu Kα) = 5.960 mm^{-1}, 20 312 reflections measured, 17 608 unique (R_{int} = 0.133) were used in the calculations. Absolute structure parameter was 0.04(1). The final $R_1(F^2)$ was 0.1281.

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Supporting Information Available: Crystallographic data in CIF format for compound **1′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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