

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

Received January 16, 2006

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 ligands¹ 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

[†] 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.

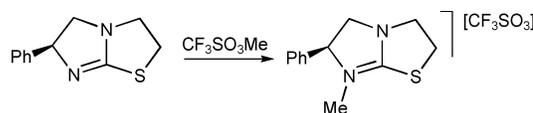
(1) Selected reviews on complexes having NHC ligands: (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. (b) Arduengo, A. *Acc. Chem. Res.* **1999**, *32*, 913. (c) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (d) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617–618*, 70. (e) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (f) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247.

(2) Reviews on catalytic applications of complexes having NHC ligands: (a) Ref 1e. (b) Trnka, M. T.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (c) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry*, **2003**, *14*, 951. (d) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239. (e) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69. (f) César, V.; Bellemin-Laponnaz, S.; Gade L. H. *Chem. Soc. Rev.* **2004**, *33*, 619.

(3) Examples of catalytic applications of complexes with chiral NHC ligands: (a) César, V.; Bellemin-Laponnaz, S.; Wadepohl, H. H.; Gade L. H. *Chem. Eur. J.* **2005**, *11*, 2862. (b) Chianese, A. R.; Crabtree, R. H. *Organometallics* **2005**, *24*, 4432. (c) Clavier, H.; Coutable, L.; Toupet, L.; Guillemain, J. C.; Mauduit, M. *J. Organomet. Chem.* **2005**, *690*, 5237. (d) Song, C.; Ma, C.; Ma, Y.; Feng, W.; Ma, S.; Chai, Q.; Merritt, M. B. *Tetrahedron Lett.* **2005**, *46*, 3241. (e) van Veldhuizen, J. J.; Campbell, J. E.; Hoveyda, R. E.; Amir, H. *J. Am. Chem. Soc.* **2005**, *127*, 6877. (f) Kremzow, D.; Seidel, G.; Lehmann, C. W.; Fuerstner, A. *Chem. Eur. J.* **2005**, *11*, 1833. (g) Focken, T.; Rudolph, J.; Bolm, C. *Synthesis* **2005**, 429. (h) Bonnet, L. G.; Douthwaite, R. E.; Kariuki, B. M. *Organometallics* **2003**, *22*, 4187. (i) Costabile, C.; Cavallo, L. *J. Am. Chem. Soc.* **2004**, *126*, 9592.

(4) Further examples of complexes with chiral NHC ligands: (a) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R.; Houghton, J.; Kariuki, B. M.; Simonovic, S. *Dalton Trans.* **2004**, 3528. (b) Gischig, S.; Togni, A. *Organometallics* **2004**, *23*, 2479. (c) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R. *Organometallics* **2003**, *22*, 4384. (d) Glorius, F.; Altenhoff, G.; Goddard, R.; Lehmann, C. *Chem. Commun.* **2002**, 2704.

Scheme 1



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.

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 anthelmintic⁵ and anticancer⁶ properties.

Results and Discussion

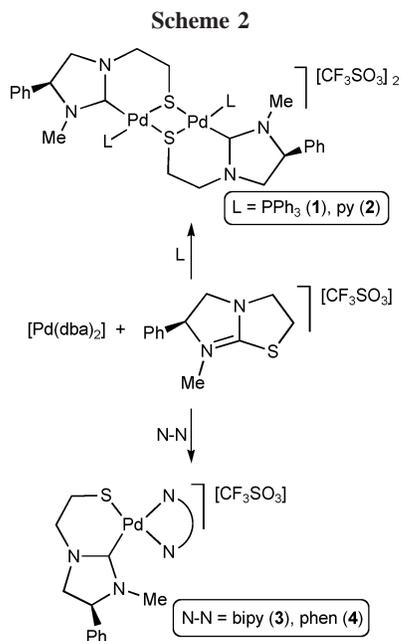
Methyl levamisolium triflate was made in quantitative yield treating levamisole with methyl triflate (Scheme 1). Levamisole was conveniently prepared by deprotonation of commercial levamisole hydrochloride with potassium hydroxide.

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 [Pd₂(S–C)₂(PPh₃)₂](CF₃SO₃)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 [Pd₂(S–C)₂(PPh₃)₂][BF₄]₂ (**1'**), prepared by metathesis of **1** with Na[BF₄], was determined by X-ray diffraction methods. The compound crystallizes in the chiral space group *P1*, 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-

(5) Amery, W. K. P.; Bruynseels, J. P. J. M. *Int. J. Immunopharmacol.* **1992**, *14*, 481, and references therein.

(6) Kovach, J. S.; Svingen, P. A.; Schaid, D. J. *J. Natl. Cancer Inst.* **1992**, *84*, 515, and references therein.



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 Pd₂S₂ core is not planar, since both PdS₂ 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(sp²) 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 imidazolium 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

(7) Examples of thiolate-bridged palladium complexes: (a) García-Antón, J.; Pons, J.; Solans, X.; Font-Bardía, M.; Ros, J. *Inorg. Chim. Acta* **2003**, *355*, 87. (b) Usón, M. A.; Llanos, J. M. *J. Organomet. Chem.* **2002**, *663*, 98. (c) Ruiz, J.; Giner, J.; Rodríguez, V.; López, G.; Casabó, J.; Molins, E.; Miratvilles, C. *Polyhedron* **2000**, *19*, 1627. (d) Tzeng, B. C.; Fu, W. F.; Che, C. M.; Chao, H. Y.; Cheung, K. K.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1017. (e) Ruiz, J.; Vicente, C.; Rodríguez, V.; López, G. *Polyhedron* **1998**, *17*, 1503.

(8) Examples of metal-mediated S–C bond cleavage processes: (a) Yu, K.; Li, H.; Watson, E.; Virkaitis, K. L.; Carpenter, G. B.; D. A. Sweigart, *Organometallics* **2001**, *20*, 3550. (b) Kim, Y. J.; Lee, S. C.; Cho, M. H.; Lee, S. W. *J. Organomet. Chem.* **1999**, *588*, 268. (c) Albéniz, A.; Espinet, P.; Lin, Y. S. *Organometallics* **1996**, *15*, 5010. (d) Osakada, K.; Chiva, T.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1589. (e) Dehand, J.; Jordanov, J. *J. Chem. Soc., Chem. Commun.* **1975**, 743. (f) Cabeza, J. A.; Martínez-García, M. A.; Riera, V.; Ardura, D.; García-Granda, S. *Eur. J. Inorg. Chem.* **2000**, 299. (g) Umakoshi, K.; Yamashaki, T.; Fukuoka, A.; Kawano, H.; Ichikawa, M.; Onishi, M. *Inorg. Chem.* **2002**, *41*, 4093.

(9) Reviews on the use of molecular compounds as models for HDS processes: (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61. (c) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1990**, *105*, 61. (d) Sánchez-Delgado, R. *J. Mol. Catal.* **1994**, *86*, 287. (e) Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1996**, 801. (f) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073.

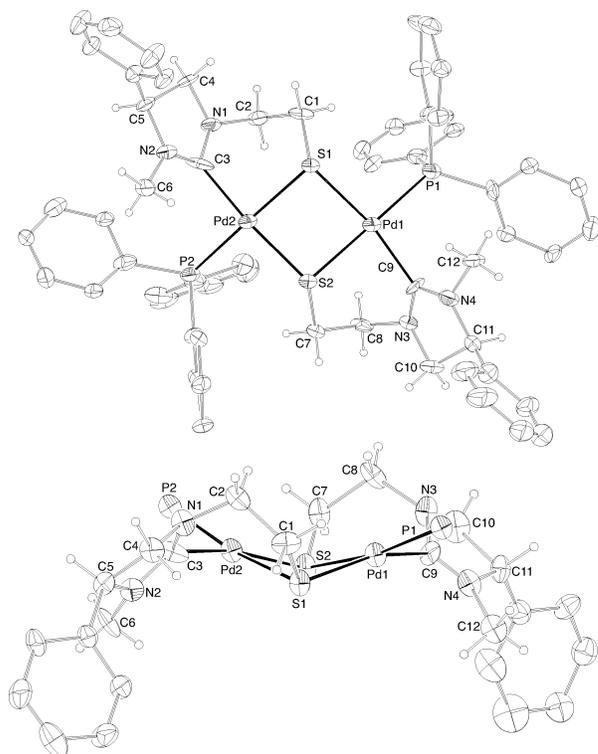


Figure 1. Structure of one of the two independent dications found in the unit cell of **1**, viewed approximately along the noncrystallographic 2-fold axis (top) and along the S(1)–S(2) vector (bottom). The PPh₃ phenyl groups of the bottom view and all the phenyl hydrogen atoms have been omitted for 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).

resulted in mixtures of compound **1** with a complex containing two PPh₃ ligands, characterized by having two doublets in its ³¹P{¹H} NMR spectrum ($\delta = 21.3$ and 23.5 , $J = 33$ Hz), and probably corresponding to the formula [Pd(S–C)(PPh₃)₂]CF₃SO₃ (vide infra). Unfortunately, this complex could not be isolated pure because it slowly releases one phosphine ligand in solution to give compound **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 [Pd₂(S–C)₂(py)₂](CF₃SO₃)₂ (**2**) and [Pd(S–C)(N–N)]CF₃SO₃ (**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 SCH₂ 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 bifunctional mononuclear derivatives of the S–C ligand. In the ¹³C{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 levamisolium (lvms) have been reported. They are the complexes [MCl₂(lvms)₂] (M =

Co, Ni, Cu, Zn),¹⁰ [Pd(aminoacido)(lvms)]Cl,¹¹ and [PtCl(en)(lvms)]Cl (en = ethylenediamine),¹² which all have the levamisole ligand coordinated through the sp² 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(sp²) 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 sp² 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 (¹H ³¹P) and AV-400 (¹³C); room temperature; TMS as internal standard for ¹H, solvent resonance as internal standard for ¹³C, and aqueous 85% H₃PO₄ as external standard for ³¹P. 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 C₁₁H₁₂N₂S (204.29): C, 64.67; H, 5.92; N, 13.71. Found: C, 64.40; H, 5.91; N, 13.72. Specific rotation: [α]_D –105 (c 0.01, 298 K, CH₂Cl₂). ¹H NMR (300 MHz, 293 K, CD₂Cl₂): 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). ¹³C{¹H} NMR (100.6 MHz, DEPT, 293 K, CD₂Cl₂): δ 174.7 (C), 143.3 (C), 128.9 (2 CH), 127.6 (CH), 126.9 (2 CH), 77.3 (CH), 58.8 (CH₂), 49.5 (CH₂), 34.5 (CH₂).

(10) (a) Kovachev, T. B.; Stamberov, P. N.; Ivanov, D. S.; Mitcheva, M. K.; Marinova, S. P.; Astroug, H. A.; Stoychkov, J. N. *Pharmazie* **1994**, *49*, 25. (b) Cabeza, J. A.; del Río, I.; Sánchez-Vega, M. G.; García-Granda, S. *Acta Crystallogr.* **2005**, *E61*, m1984.

(11) Nijasure, A. M.; Joshi, V. N.; Savant, A. D. *J. Inorg. Biochem.* **1999**, *73*, 109.

(12) Arvanitis, G. M.; Bernardini, M. E.; Parkinson, G. N.; Schneider, B. S. *Acta Crystallogr.* **1993**, *C49*, 1246.

(13) Cabeza, J. A.; del Río, I.; García-Granda, S.; Riera, V.; Sánchez-Vega, M. G. *Eur. J. Inorg. Chem.* **2002**, 2561.

(14) Rettig M. F.; Maitlis, P. M. *Inorg. Synth.* **1990**, *28*, 110.

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 C₁₃H₁₅F₃N₂O₃S (366.33): C, 46.42; H, 4.50; N, 8.33. Found: C, 46.29; H, 4.58; N, 8.29. Specific rotation: [α]_D –102 (c 0.01, 298 K, CH₂Cl₂). ¹H NMR (300 MHz, 293 K, CD₂Cl₂): 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). ¹³C{¹H} NMR (100.6 MHz, DEPT, 293 K, CD₂Cl₂): 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 (CH₂), 48.9 (CH₂), 37.0 (CH₂), 33.7 (CH₃).

[Pd₂(S–C)₂(PPh₃)₂](CF₃SO₃)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 C₆₂H₆₀F₆N₄O₆P₂S₄ (1474.09): C, 50.51; H, 4.10; N, 3.80. Found: C, 50.63; H, 4.18; N, 3.68. ¹H NMR (300 MHz, 293 K, CDCl₃): 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). ³¹P{¹H} NMR (121.5 MHz, 293 K, CDCl₃): δ 28.0 (s). ¹³C{¹H} NMR (100.6 MHz, DEPT, 293 K, CDCl₃): 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 (CH₂), 54.7 (CH₂), 34.9 (Me), 27.5 (CH₂).

[Pd₂(S–C)₂(py)₂](CF₃SO₃)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 C₃₆H₄₀F₆N₆O₆Pd₂S₄ (1107.84): C, 39.03; H, 3.64; N, 7.59. Found: C, 39.18; H, 3.77; N, 7.48. ¹H NMR (300 MHz, 293 K, CDCl₃): 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). ¹³C{¹H} NMR (100.6 MHz, DEPT, 293 K, CDCl₃): 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 (CH₂), 53.0 (CH₂), 35.5 (Me), 25.8 (CH₂).

[Pd(S–C)(bipy)]CF₃SO₃ (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

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 - CF₃SO₃]. ¹H NMR (300 MHz, 293 K, CDCl₃): 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). ¹³C{¹H} NMR (100.6 MHz, DEPT, 293 K, CDCl₃): 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 (CH₂), 54.9 (CH₂), 35.6 (Me), 26.7 (CH₂).

[Pd(S-C)(phen)]CF₃SO₃ (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 - CF₃SO₃]. ¹H NMR (300 MHz, 293 K, CDCl₃): 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). ¹³C{¹H} NMR (100.6 MHz, DEPT, 293 K, CDCl₃): δ 191.6 (C), 155.7 (CH), 149.1 (CH), 147.0 (C), 145.9 (C), 139.6 (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 (CH₂), 55.1 (CH₂), 35.7 (Me), 26.6 (CH₂).

Preparation of Tetrafluoroborate 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 [Pd₂(S-C)₂(PPh₃)₂](BF₄)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 $C_{60}H_{60}B_2$ -

$F_8N_4P_2Pd_2S_2$ (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 [Pd₂(S-C)₂(PPh₃)₂](BF₄)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 K α 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 *P1*, 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 system¹⁸ 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, $\alpha = 81.075(4)^\circ$, $\beta = 88.287(5)^\circ$, $\gamma = 63.849(4)^\circ$, $U = 3298.5(5)$ Å³, $T = 200(2)$ K, space group *P1*, $Z = 2$, $\mu(\text{Cu K}\alpha) = 5.960$ mm⁻¹, 20 312 reflections measured, 17 608 unique ($R_{\text{int}} = 0.133$) were used in the calculations. Absolute structure parameter was 0.04(1). The final $R_1(F^2)$ was 0.1281.

Acknowledgment. This work has been supported by the Spanish MCyT-MEC (project BQU2002-02623). The University of Carabobo (Venezuela) is acknowledged for a research grant to M.G.S.-V.

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>.

OM060042H

(15) Beurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; García-Granda, S.; Gould, R. O.; Israël, R.; Smits, J. M. M. *The DIRDIF-96 Program System*; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1996.

(16) Sheldrick, G. M. *SHELXL97*, Version 97-2; University of Göttingen: Göttingen, Germany, 1997.

(17) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; University of Utrecht: Utrecht, The Netherlands, 2003.

(18) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.