Palladium Complexes of Chiral Planar 1-Phosphino-2-sulfenylferrocenes as Efficient Catalysts in Enantioselective Diels−Alder Reactions

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The readily available dichloride palladium complexes of chiral planar (*R*)-1-phosphino-2-sulfenylferrocenes (Fesulphos ligands) act as efficient Lewis acids in the catalytic asymmetric Diels−Alder reaction of cyclopentadiene with acryloyl-1,3-oxazolidin-2-one. Very high enantioselectivities, up to 95% ee, have been reached from Fesulphos ligands having a very bulky substitution at both sulfur and phosphorus coordinating atoms.

Introduction

The asymmetric Diels−Alder (ADA) reaction constitutes a fundamental C−C bond forming reaction in modern organic synthesis. Therefore, the search for new chiral Lewis acids as catalysts for this transformation has received a great deal of attention in recent years,[1] the reaction of cyclopentadiene with the bidentate acryloyl oxazolidinone becoming the standard bench reaction for the evaluation of the efficiency of such catalysts. Among many catalyst systems identified to date, the vast majority are based on C_2-symmetric chiral bidentate ligands having O,O- (e.g., BINOL derivatives),[2] N,N- (e.g., bis-oxazolines),[3] or P,P-coordination modes (e.g., BINAP).[4]

As an alternative, mixed donor ligands with strong electronic differentiation have also provided high asymmetric inductions, most precedents involving the use of P,N-bidentate chiral ligands, especially phosphino-oxazolines.[5] However, the many applications of bidentate P,N-ligands found in asymmetric metal-catalyzed reactions[6] contrast with the much less studied chiral thioethers with potential P,S-coordination, despite the appealing fact that the sulfur atom becomes stereogenic upon coordination with the transition metal, therefore imposing a unique asymmetric environment in very close proximity to the reactive metal center.[7] Concerning the ADA, to the best of our knowledge, there was a single reported catalyst based on P,S-coordination: the cationic palladium complexes of chiral phosphino-oxatiane ligands described by Nakano et al.[8]

We have recently described a highly tunable family of P,S-bidentate ligands possessing planar chirality as the only element of asymmetry: the 1-phosphino-2-sulfenylferrocenes (Fesulphos, **1**).[9] This new family of chiral ligands, especially those having a bulky substitution at sulfur, have provided very high asymmetric inductions in some Pd-catalyzed reactions, such as allylic substitutions[9b] and the desymmetrization of oxabenzonorbornadienes with dialkylzinc reagents.[10] In

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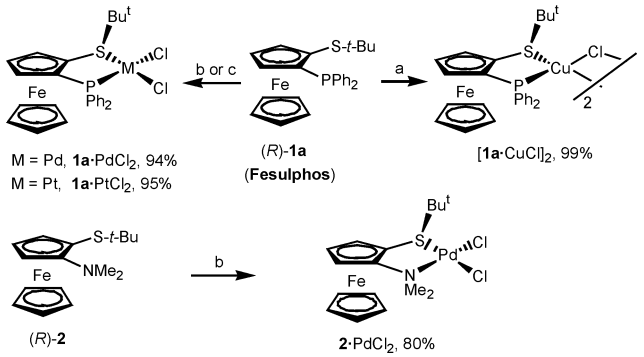
Scheme 1. Preparation of Metal Complexes of 1-Phosphino- and 1-(Dimethylamino)-2-sulfenylferrocenes[a]



[a] (a) CuCl, THF-MeOH, rt. (b) $Pd(CH_3CN)_2Cl_2$, CH_2Cl_2, rt. (c) $PtCl_2$, CH_2Cl_2, rt.

addition, these ligands have also proved to be very efficient in the enantioselective Cu-catalyzed reaction of Danishefsky's diene with *N*-sulfonylimines.[11] Extending the interest of Fesulphos in enantioselective catalysis, we report herein that metal complexes of such ligands, especially their palladium complexes, act as effective catalysts in the ADA reaction of cyclopentadiene with acryloyl oxazoline.

Results and Discussion

Initially, we chose as parent ligand (*R*)-1-diphenylphosphino-2-*tert*-butylsulfenylferrocene [(*R*)-**1a**]. Due to the high affinity of sulfur to late transition metals, we focused our attention on its copper(I), palladium(II), and platinum(II) chloride complexes as precursors of the required cationic Lewis acid catalyst. These metal complexes were readily prepared in nearly quantitative yield by straightforward treatment of **1a** with CuCl,[11] $Pd(CH_3CN)_2Cl_2$,[9b] and $PtCl_2$, respectively. For comparison purposes, the Pd complex of the related N,S-ligand (*R*)-1-(dimethylamino)-2-*tert*-butylsulfenylferrocene[12] (**2**·$PdCl_2$) was also prepared following the same procedure (Scheme 1). Interestingly, a single epimer at sulfur was detected by NMR in the four complexes: the one placing the bulky *tert*-butyl group in anti arrangement with regard to the ferrocene unit [(R_P,R_S) configuration].[13] In addition, the chloride-bridged dimer complex [**1a**·CuCl]$_2$ was obtained as a single isomer, the two phosphines being located at the same face of the molecule and the two sulfides at the opposite face with the *tert*-butyl groups oriented anti with regard to each other (Figure 1).

This configuration was unequivocally determined by X-ray diffraction of [**1a**·CuCl]$_2$,[14] **1a**·$PdCl_2$,[15] and **1a**·$PtCl_2$[16] (Figure 1). Among other interesting structural information deduced from this crystallographic study, it should be noted the following four features: (a) very similar and nearly planar conformation of the P,S-five-membered metallacycle is found in all the studied metal complexes,[17] determining a high steric hindrance of the upper face of the metallacycle due to the up orientation of the *tert*-butyl group and one of the phenyl groups at phosphorus; (b) the slightly distorted tetrahedral structure of the Cu(I) complex [θ S−Cu−Cl(1) = 113.6°, θ P−Cu−Cl(1A) = 124.9°]; (c) the perfect square planar geometry around the metal center in the case of the Pd (sum of angles around Pd = 360.2°) and Pt complexes (sum of angles around Pt = 360.0°); (d) the great electronic trans effect exerted by the phosphorus donor atom, compared to the sulfur moiety, in the case of the square planar complexes. For instance, in **1a**·$PdCl_2$ and **1a**·$PtCl_2$ the M−Cl bond trans to phosphorus is much longer (2.346 and 2.352 Å, respectively) than that trans to sulfur (2.302 and 2.308 Å, respectively).

In Table 1 are summarized the results obtained in the standard ADA reaction of cyclopentadiene with acryloyl-1,3-oxazolidin-2-one in the presence of 10 mol % of the dichloride metal complex and 20 mol % of $AgBF_4$ as chloride scavenger to promote the in situ generation of the presumed catalytically active dicationic Lewis acid. The reactions were conducted in CH_2Cl_2 as optimal solvent,[18] in the presence of molecular sieves,[19] and at the lowest temperature to allow them to reach quantitative conversion.[20]

As expected, all ADA reactions were highly endo selective, although very different asymmetric induction was observed from these complexes. Thus, while the Pt complex (entry 2) was the least reactive and enantioselective, providing the Diels−Alder adduct **3** in racemic

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(13) This high control in the formation of the stereogenic sulfur atom seems to rely on steric effects. Thus, ligands with a less bulky substituent at sulfur, such as a *p*-tolyl group instead of the *tert*-butyl group, provided mixtures of epimers at sulfur upon complexation with the metal. For instance, the reaction of 1-diphenylphosphino-2-*p*-tolylsulfenylferrocene with $Pd(CH_3CN)_2Cl_2$ afforded a 5:1 mixture of epimers at sulfur.

(14) Reported in ref 11. Crystal data for $C_{52}H_{54}Cl_2Cu_2Fe_2P_2S_2$·$CH_2Cl_2$ [**1a**·CuCl]$_2$: crystal size 0.38 × 0.36 × 0.34 mm^3, M_w = 1202.95, trigonal, space group *P*3(2)21, a = 17.7079(2) Å, b = 17.7079(2) Å, c = 15.0264(2) Å, α = 90°, β = 90°, γ = 120°, V = 4080.56(8) Å^3, Z = 3, D_c = 1.469 g cm^{-3}, μ = 8.413 mm^{-1}, T = 296(2) K, Cu Kα radiation (λ = 1.54178 Å), 24 724 reflections measured, 5090 independent (R_{int} = 0.0718). Refinement on F^2 for 5090 reflections and 304 parameters gave GOF = 1.072, R = 0.0360, R_w = 0.0911 for $I > 2\sigma(I)$.

(15) Reported in ref 9. Crystal data for $C_{26}H_{27}Cl_2FePPdS$ [**1a**·$PdCl_2$]: crystal size 0.08 × 0.25 × 0.25 mm^3, M_w = 635.66, monoclinic, space group $P2_1/n$, a = 9.7541(5) Å, b = 15.9433(8) Å, c = 16.9386(8) Å, α = 90°, β = 94.8180(10)°, γ = 90°, V = 2624.9(2) Å^3, Z = 4, D_c = 1.609 g cm^{-3}, μ = 1.595 mm^{-1}, T = 296(2) K, Mo Kα radiation (λ = 0.7173 Å), 17 617 reflections measured, 7447 independent (R_{int} = 0.0810). Refinement on F^2 for 7447 reflections and 293 parameters gave GOF = 1.067, R = 0.0515, R_w = 0.1076 for $I > 2\sigma(I)$. CCDC reference number 185296.

(16) Crystal data for $C_{26}H_{27}Cl_2FePPtS$·CH_2Cl_2 [**1a**·$PtCl_2$]: crystal size 0.25 × 0.15 × 0.15 mm^3, M_w = 809.27, triclinic, space group $P1/n$, a = 10.19170(10) Å, b = 10.53430(10) Å, c = 14.0443(2) Å, α = 82.5820(10)°, β = 80.6780(10)°, γ = 70.0560(10)°, V = 1453.31(3) Å^3, Z = 2, D_c = 1.849 g cm^{-3}, μ= 17.568 mm^{-1}, T = 296(2) K, Cu Kα radiation (λ = 1.54178 Å), 9358 reflections measured, 7024 independent (R_{int} = 0.0252). Refinement on F^2 for 7024 reflections and 638 parameters gave GOF = 1.048, R = 0.0375, R_w = 0.0952 for $I > 2\sigma(I)$. CCDC reference number 237743. Two slightly different structures were detected in the crystal, differing mainly in the torsion angle of the unsubstituted Cp ring (Φ = −38.474 and −17.440).

(17) The copper complex deviates slightly from the pseudo-planarity of the P,S-five membered metallacycle: θ Cu−S−C_{Cp}−C_{Cp} = 8.9° (for [**1a**·CuCl]$_2$), θ Pd−S−C_{Cp}−C_{Cp} = 0.1° (for **1a**·$PdCl_2$), θ Pt−S−C_{Cp}−C_{Cp} = 5.6° (for **1a**·$PtCl_2$).

(18) In other solvents such as toluene, THF, and acetonitrile the reactivity or/and the enantioselectivity were much lower.

(19) In the absence of molecular sieves the reaction did not go to completion, likely due to the deactivation of the cationic Lewis acid with traces of water.

(20) The enantioselectivity of the process strongly decreases at higher temperatures, likely because of the competitive silver-catalyzed non-enantioselective reaction. For instance, the reaction of **1a**·$PdCl_2$ at −20 °C, instead of −78 °C, afforded (*R*)-**3** with only 20% ee.

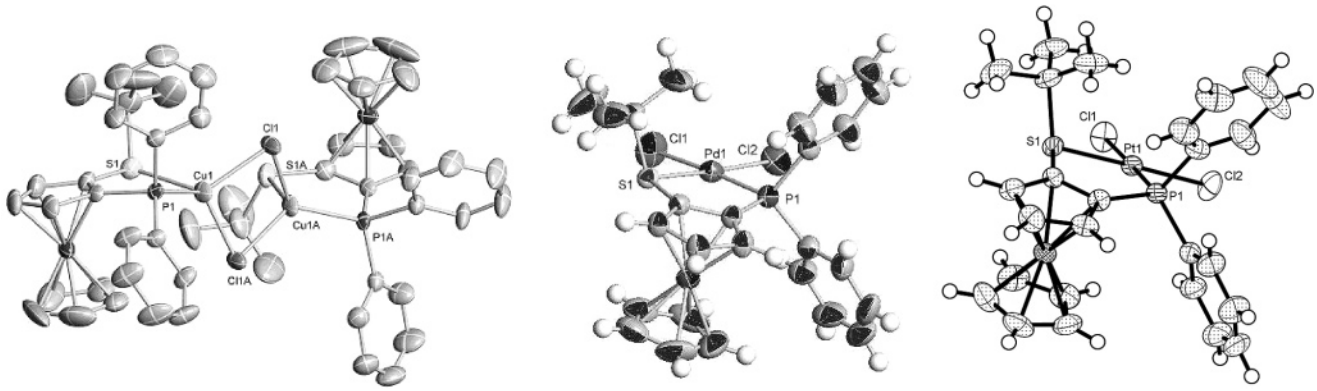
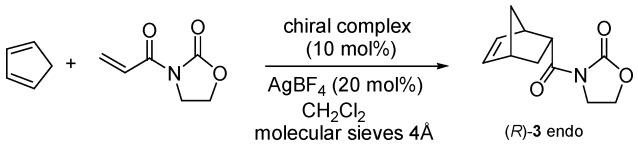


Figure 1. ORTEP plots for [**1a**·CuCl]$_2$, **1a**·PdCl$_2$, and **1a**·PtCl$_2$ (30% thermal ellipsoids) showing the atomic numbering of selected atoms. The hydrogen atoms in [**1a**·CuCl]$_2$ have been omitted for clarity. Selected bond lengths (Å) and angles (deg) of [**1a**·CuCl]$_2$: Cu1−S1 = 2.5785(9), Cu1−P1 = 2.2075(7), Cu1−Cl1 = 2.3303(7), Cu1−Cl1A = 2.3621(8); P1−Cu1−S1 = 89.67(3), P1−Cu1−Cl1 = 126.09(3), P1−Cu1−Cl1A = 124.87(3), S1−Cu1−Cl1 = 113.64(3), S1−Cu1−Cl1A = 106.63(3), Cl1−Cu1−Cl1A = 95.31(3). Selected bond lengths (Å) and angles (deg) of **1a**·PdCl$_2$: Pd1−S1 = 2.3137(9), Pd1−P1 = 2.2427(9), Pd1−Cl1 = 2.3461(11), Pd1−Cl2 = 2.3022(11); P1−Pd1−S1 = 90.83(3), P1−Pd1−Cl1 = 176.95(4), P1−Pd1−Cl2 = 88.26(4), S1−Pd1−Cl1 = 89.39(4), Cl2−Pd1−S1 = 176.23(4), Cl2−Pd1−Cl1 = 91.72(5). Selected bond lengths (Å) and angles (deg) of **1a**·PtCl$_2$: Pt1−S1 = 2.2928(18), Pt1−P1 = 2.2209(19), Pt1−Cl1 = 2.352(2), Pt1−Cl2 = 2.308(2); P1−Pt1−S1 = 90.56(7), P1−Pt1−Cl1 = 178.65(8), P1−Pt1−Cl2 = 91.32(8), S1−Pt1−Cl1 = 88.21(8), S1−Pt1−Cl2 = 177.68(8), Cl2−Pt1−Cl1 = 89.89(8).

Table 1. ADA Reaction of Cyclopentadiene with *N*-Acryloyl Oxazolidinone in the Presence of Fesulphos Metal Complexes

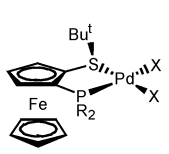


entry	complex	T (°C)	time (days)	yield (%)[a]	endo/exo[b]	ee (%)[c] (conf)
1	[**1a**·CuCl]$_2$	−20	0.7	94	95/5	25 (*S*)
2	**1a**·PtCl$_2$	−20	1	91	90/10	0
3	**1a**·PdCl$_2$	−78	6	69	95/5	67 (*R*)
4	**2**·PdCl$_2$	−78	6	20[d]	95/5	38 (*R*)
5	**1b**·PdCl$_2$	−50	6	79	91/9	>2
6	**1c**·PdCl$_2$	−78	6	66	90/10	62 (*R*)
7	**1d**·PdCl$_2$	−50	6	83	93/7	74 (*R*)
8	**1e**·PdCl$_2$	−78	6	35[d]	96/4	80 (*R*)
9	**1f**·PdCl$_2$	−78	1.6	90	98/2	95 (*R*)
10[e]	**1f**·PdBr$_2$	−78	7	90	97/3	90 (*R*)
11	[**1f**·CuBr]$_2$	−78	6	87	99/1	54 (*S*)

[a] In pure product after chromatography. [b] Measured by ^{1}H NMR. [c] Determined by HPLC (Chiralcel OD column). [d] Conversion yield. [e] Using AgOTf (20 mol %).

form, the reaction of the Cu complex (entry 1) yielded (*S*)-**3** in a low 25% ee. By contrast, the Pd complexes (entries 3 and 4) were much more reactive, allowing performing the reaction at −78 °C, which produced the enantiomeric adduct (*R*)-**3** as the major product. The highest asymmetric induction was obtained in the case of the P,S-complex **1a**·PdCl$_2$ (67% ee).

Having concluded from this study the superiority of the P,S-palladium coordination[21,22] over other types of P,S-metal complexes and N,S-ligands, we next undertook the optimization of the enantioselectivity of the process by studying the effect of the substitution at phosphorus (entries 5−10 in Table 1). All complexes **1**·PdCl$_2$ (Figure 2) were readily prepared as single epimers at sulfur from ligands **1** and Pd(CH$_3$CN)$_2$Cl$_2$ following the same procedure as previously described for **1a**·PdCl$_2$.[9b] In a similar way **1f**·PdBr$_2$ was isolated in 94% yield by reaction of **1f** with Pd(CH$_3$CN)$_2$Br$_2$. Figure 3 shows the X-ray crystal structure of the complex **1e**·PdCl$_2$,[23] proving the bidentate character of the Fesulphos ligands even when bearing very bulky groups at both sulfur (*tert*-butyl) and phosphorus (α-naphthyl) atoms. As minor structural differences between this complex and the parent complex **1a**·PdCl$_2$, it should be noted the elongation of the Pd−P bond (2.270 vs 2.243 Å) and the slight opening of the P−Pd−Cl(2) angle (93.7° vs 88.3°) as the result of the important increase in the steric bulkiness around the phosphorus atom.



R = Ph, **1a**·PdCl$_2$, 94%
R = α-Fur, **1b**·PdCl$_2$, 99%
R = Cy, **1c**·PdCl$_2$, 99%
R = (*p*-F)C$_6$H$_4$, **1d**·PdCl$_2$, 99%
R = α-Naph, **1e**·PdCl$_2$, 78%
R = *o*-Tol, **1f**·PdCl$_2$, 99%
R = *o*-Tol, **1f**·PdBr$_2$, 94%

Figure 2. Fesulphos palladium(II) halide complexes prepared by reaction of the P,S-ligand with Pd(CH$_3$CN)$_2$X$_2$ in CH$_2$Cl$_2$ at room temperature.

Evaluation of this set of Fesulphos palladium complexes in the ADA reaction led us to find that the enantioselectivity was deeply affected by the electronic and steric properties of the phosphine moiety (Table 1).

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(22) For a recent review on enantioselective Pd-catalyzed transformations, see: Tietze, L. F.; Ila, H.; Bell, H. P. *Chem. Rev*. **2004**, *104*, 3453.

(23) Crystal data for C$_{34}$H$_{31}$Cl$_2$FePPdS [**1e**·PdCl$_2$]: crystal size 0.28 × 0.20 × 0.15 mm^3, M_w = 735.77, orthorhombic, space group $P2(1)2(1)2(1)/n$, a = 10.68560(10) Å, b = 16.15590(10) Å, c = 17.8511(2) Å, α = 90°, β = 90°, γ = 90°, V = 3081.75(5) Å^3, Z = 4, D_c = 1.586 g cm^{-3}, μ = 11.371 mm^{-1}, T = 297(2) K, Cu Kα radiation (λ = 1.54178 Å), 9358 reflections measured, 5687 independent (R_{int} = 0.0469). Refinement on F^2 for 5687 reflections and 364 parameters gave GOF = 1.048, R = 0.0313, R_w = 0.0804 for $I > 2\sigma(I)$. CCDC reference number 237744.

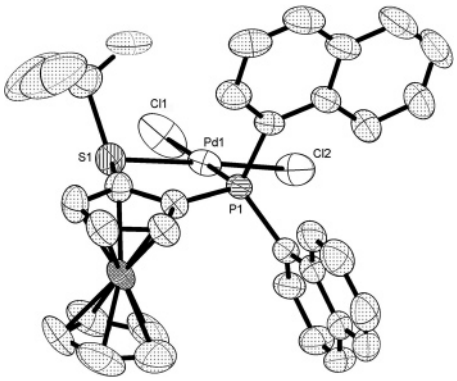

Figure 3. ORTEP plot for **1e**·$PdCl_2$ (30% thermal ellipsoids) showing the atomic numbering of selected atoms. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−S1 = 2.3015(11), Pd1−P1 = 2.2703(9), Pd1−Cl1 = 2.3484(13), Pd1−Cl2 = 2.3015(11); P1−Pd1−S1 = 90.38(3), P1−Pd1−Cl1 = 175.64(5), P1−Pd1−Cl2 = 93.73(4), S1−Pd1−Cl1 = 85.49(5), Cl2−Pd1−S1 = 174.97(5), Cl2−Pd1−Cl1 = 90.47(6).

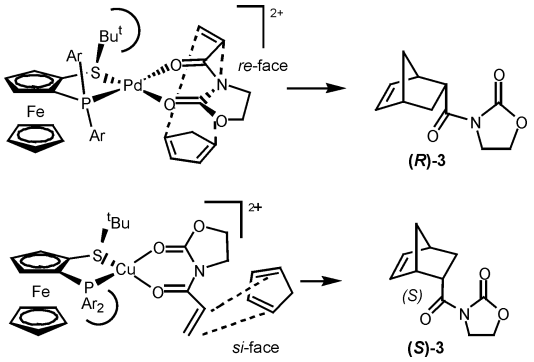

Figure 4. Proposed models for the ADA reaction.

Electronically rich phosphines (complexes of ligands **1b** and **1c**) were found to have a deleterious effect on the enantioselectivity (entries 5 and 6), especially in the case of the furyl phosphine **1b**. In contrast, complexes with electronically poor phosphine **1d** (entry 7) and, particularly, the bulky phosphines **1e** and **1f** (entries 8−9) produced a substantial enhancement of the asymmetric induction. Considering both reactivity and enantioselectivity, the best result was obtained from the complex of the *o*-tolyl phosphine **1f** (entry 9), which afforded the endo cycloadduct (*R*)-**3** in excellent chemical yield (90%) and enantioselectivity (95% ee). In agreement with the presumed participation of a cationic palladium complex as the active catalyst of the process, a similar result was obtained from the dibromo complex **1f**·$PdBr_2$ and AgOTf as halogen scavenger (entry 10, 90% ee).[24]

For the optimal Fesulphos ligand **1f** we confirmed the superiority of the Pd complex over its Cu(I) complex. Thus, the ADA reaction catalyzed by [**1f**·CuBr]$_2$/$AgBF_4$[25] provided the adduct **3** in a moderate 54% ee, albeit, interestingly, with opposite enantioselectivity (entry 11).

Assuming a bidentate coordination of the dienophile to the electrophilic metal center, Figure 4 shows a tentative stereochemical model for these ADA reactions based on the different geometry of the palladium (square planar) and copper (tetrahedral) complexes of Fesulphos ligands. The endo approach of cyclopentadiene to the least hindered face of the dienophile, avoiding the steric interaction with the *tert*-butyl group at sulfur and the bulky aryl groups at phosphorus, could explain the opposite sense of enantioselectivity displayed by the Pd (*re*-face approach) and Cu complexes (*si*-face approach).[26]

In summary, the P,S-bidentate character of Fesulphos ligands (**1**) has been proved by X-ray diffraction analysis of several metal complexes. By tuning the substitution at phosphorus, the palladium catalysts derived from Fesulphos ligands afforded high enantioselectivities, up to 95% ee, in the ADA reaction of cyclopentadiene with *N*-acryloyl-1,3-oxazolidin-2-one. Interestingly, the opposite enantioselectivity observed from Pd and Cu complexes of Fesulphos ligands could be due to the different geometry around the metal center. The study of the effectiveness of these novel P,S-palladium Lewis acids in other types of cycloadditions is underway.

Experimental Section

NMR spectra were recorded on a Bruker AC-200 [200 MHz (^{1}H), 50 MHz (^{13}C)] or AC-300 [300 MHz (^{1}H), 75 MHz (^{13}C)] at room temperature in $CDCl_3$ with internal $CHCl_3$ as the reference (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). For phosphorus- and fluoro-containing compounds the observed list of peaks is given as the ^{13}C NMR data, except for those cases where the J_{P-C} has been unequivocally determined. Mass spectra (MS) were determined on a HP-5985 mass spectrometer under FAB conditions. All reactions were carried out in anhydrous solvents and under argon atmosphere. CH_2Cl_2 was dried and stored over microwave-activated 4 Å molecular sieves. Single crystals of the four compounds were grown by slow diffusion of hexane onto dichloromethane solutions. Data collections were carried out at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Cu Kα (λ = 1.54178 Å) or Mo Kα (λ = 0.7173 Å) and $2\theta/\omega$ scans method. Absorption correction method SADABS (v. 2.03) was applied, except for **1a**·$PdCl_2$. All structures were solved by direct methods (SHELXS-97), and the refinement was made by full-matrix least-squares on F^2 (SHELXL-97).

General Procedure for the Synthesis of Dichloro and Dibromo Palladium Complexes [LPdX$_2$].[9b] A solution of **1** or **2** (0.5 mmol) and $Pd(CH_3CN)_2Cl_2$ or $Pd(CH_3CN)_2Br_2$ (0.5 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h at room temperature under argon atmosphere. After concentration under reduced pressure, the resulting solid was triturated with Et_2O, filtered, and air-dried to afford complex **LPdX$_2$**.

(R_P,R_S)-{1-(*tert*-Butylsulfenyl)-2-[bis-(*o*-tolyl)phosphino]-ferrocene}(dichloro)palladium(II) [1f·PdCl$_2$]. Yield: 99%, red solid; $[\alpha]^{20}_D$ −255° (*c* 0.10, $CHCl_3$); mp >200 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.40−9.22 (m, 1H), 7.58−7.45 (m, 2H), 7.40−7.30 (m, 1H), 7.25−7.14 (m, 2H), 7.12−6.90 (m, 2H), 5.03 (s, 1H), 4.94 (s, 1H), 4.29 (s, 1H), 4.15 (s, 5H), 2.45 (s, 3H), 1.93 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.5 (d, J_{P-C} = 11.5 Hz), 140.4, 140.1, 139.9, 132.3, 132.2, 132.1, 131.8, 131.7, 131.5, 131.4, 131.3, 131.1, 126.4, 126.2, 126.1, 125.8, 125.7, 125.3, 86.4, 86.0, 85.9, 85.2, 80.2 (d, J_{P-C} = 5.2 Hz), 75.5 (d, J_{P-C} = 11.5 Hz), 72.6, 70.8, 59.8, 31.8, 23.5 (d, J_{P-C} = 4.2 Hz), 22.3 (d, J_{P-C} = 3.1 Hz). MS (FAB+): *m/z* 629 (M^+ + H − Cl, 6), 591 (16), 534 (17), 307 (24), 154 (100). Anal. Calcd for $C_{28}H_{31}Cl_2FePPdS$·$2CH_2Cl_2$: C, 42.45; H, 4.18; S, 3.91. Found: C, 42.29; H, 4.08; S, 3.80.

(24) $AgBF_4$ provided a similar reactivity (84% yield), although the enantioselectivity was somewhat lower (78% ee).

(25) [**1f**·CuBr]$_2$ was prepared in 95% yield by treatment of **1f** with CuBr in THF/MeOH.

(26) Examples of reversed enantioselectivities depending on the geometry of the metal center have been previously described; see for instance: Evans, D. A.; Johnson, J. S.; Burgey, C. S.; Campos, K. R. *Tetrahedron Lett.* **1999**, *40*, 2879.

(R_P,R_S)-{1-(*tert*-Butylsulfenyl)-2-[bis-(*o*-tolyl)phosphino]-ferrocene}(dibromo)palladium(II) [1f·$PdBr_2$]. Yield: 94% (1:8 mixture of 2 rotamers at 25 °C); red solid; $[\alpha]^{20}_D$ −548° (*c* 0.02, $CHCl_3$); mp >200 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): major rotamer, δ 9.45−9.25 (m, 1H), 7.60−7.42 (m, 2H), 7.40−7.27 (m, 1H), 7.25−7.15 (m, 2H), 7.15−6.93 (m, 2H), 5.01 (s, 1H), 4.92 (t, 1H, J = 2.3 Hz), 4.25 (s, 1H), 4.18 (s, 5H), 2.5 (s, 3H), 1.92 (s, 3H), 1.54 (s, 9H); representative data of minor rotamer, δ 8.90−8.70 (m, 1H), 4.98 (s, 1H), 4.54 (s, 1H), 4.39 (s, 5H), 2.00 (s, 3H), 1.91 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3 (d, J_{P-C} = 11.5 Hz), 142.0 (d, J_{P-C} = 4.2 Hz), 141.1, 140.7, 140.1, 138.9, 138.8, 138.5, 137.4, 137.2, 132.5, 132.4, 132.3, 132.2, 131.9, 131.8, 131.7, 131.6, 131.5, 131.4, 131.3, 126.5, 126.2, 126.0, 125.8, 125.7, 125.4, 125.2, 87.1, 86.7, 85.9, 80.1 (d, J_{P-C} = 5.2 Hz), 79.3 (d, J_{P-C} = 4.2 Hz), 75.5 (d, J_{P-C} = 10.5 Hz), 74.7 (d, J_{P-C} = 11.5 Hz), 73.5, 73.0, 72.7, 70.6, 70.4, 65.8, 59.8, 53.4, 32.2, 31.3, 24.3, 24.2, 23.7, 23.6, 22.5. MS (FAB+) *m/z* 673 (M^+ + H − Cl, 6), 616 (7), 593 (9), 534 (13), 307 (30), 154 (100). Anal. Calcd for $C_{28}H_{31}Br_2FePPdS$: C, 44.68; H, 4.15; S, 4.26. Found: C, 44.96; H, 4.19; S, 4.27.

Preparation of Complex [1a·$PtCl_2$]. A solution of **1a** (87 mg, 0.19 mmol) and $PtCl_2$ (52 mg, 0.19 mmol) in CH_2Cl_2 (10 mL) was stirred for 24 h at room temperature under argon atmosphere. After filtration of the reaction mixture, followed by concentration under reduced pressure, the resulting solid was triturated with *n*-hexane/Et_2O (1:1), filtered, and air-dried to afford complex [**1a**·$PtCl_2$] as a yellow solid (132 mg, 95%), $[\alpha]^{20}_D$ −311° (*c* 0.10, $CHCl_3$); mp >200 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15−7.98 (m, 2H), 7.95−7.80 (m, 2H), 7.60−7.30 (m, 6H), 5.22−5.10 (m, 1H), 4.95−4.85 (m, 1H), 4.50−4.42 (m, 1H), 4.12 (s, 5H), 1.28 (s, 9H). ^{13}C NMR (75 MHz): δ 134.2 (d, J_{P-C} = 10.5 Hz), 132.2 (d, J_{P-C} = 10.5 Hz), 131.7 (d, J_{P-C} = 3.1 Hz), 131.1 (d, J_{P-C} = 3.1 Hz), 130.2, 128.8, 128.7, 128.6, 128.3, 128.2, 127.8, 87.6 (d, J_{P-C} = 27.4 Hz), 82.0 (d, J_{P-C} = 73.7 Hz), 80.3 (d, J_{P-C} = 6.3 Hz), 77.2, 72.5, 70.7 (d, J_{P-C} = 2.1 Hz), 58.5, 30.0. FAB+ MS: *m/z* 689 (M^+ + H − Cl, 10), 632 (23), 154 (100). Anal. Calcd for $C_{26}H_{27}Cl_2FePPtS$·2/3CH_2Cl_2: C, 41.01; H, 3.66; S, 4.11. Found: C, 40.65; H, 3.64; S, 4.01.

General Procedure for the Synthesis of Chiral Cu(I) Complexes.[11] A solution of ligand **1** (0.4 mmol) and CuCl or CuBr (0.41 mmol) in a 2:3 mixture of THF/MeOH (5 mL) was stirred at room temperature under argon for 5−10 min. The mixture was concentrated to dryness, a 4:1 mixture of *n*-hexane/EtOAc was added, and it was passed through a short pad of silica gel to obtain pure complexes after evaporation of the solvent under reduced pressure.

(R_P,R_S)-2-(*tert*-Butylsulfenyl)-1-(diphenylphosphino)-ferrocene Copper(I) Chloride Dimer [1a·$CuCl]_2$. Yield: 99%, orange solid; $[\alpha]^{20}_D$ −330° (*c* 0.10, $CHCl_3$); mp >200 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20−8.05 (m, 2H), 7.70 (t, J = 8.6 Hz, 2H), 7.45−7.35 (m, 3H), 7.35−7.20 (m, 3H), 4.42 (s, 1H), 4.63 (s, 1H), 4.50 (s, 1H), 4.00 (s, 5H), 1.12 (s, 9H). ^{13}C NMR (75 MHz): δ 135.2 (d, J_{P-C} = 30.3 Hz), 134.8 (d, J_{P-C} = 16.7 Hz), 134.4 (d, J_{P-C} = 34.5 Hz), 132.5 (d, J_{P-C} = 15.7 Hz), 130.0, 128.9, 128.3, 128.2, 128.1, 84.6 (d, J_{P-C} = 35.6 Hz), 78.7 (d, J_{P-C} = 46.0 Hz), 77.6, 73.3 (d, J_{P-C} = 4.2 Hz), 72.0, 71.4, 50.0, 30.3. MS (FAB+): *m/z* 1079 (M^+ + H − Cl, 32), 458 (100), 402 (50). Anal. Calcd for $C_{52}H_{54}Cl_2Cu_2Fe_2P_2S_2$·1$CH_2Cl_2$: C, 53.06; H, 4.70; S, 5.35. Found: C, 53.02; H, 4.64; S, 5.39.

Enantioselective Diels−Alder Reaction of *N*-Acryloyl-1,3-oxazolidin-2-one with Cyclopentadiene. Typical procedure: a mixture of [**1f**·$PdCl_2$] (7.3 mg, 0.011 mmol), $AgBF_4$ (4.3 mg, 0.022 mmol), and 4 Å molecular sieves (50 mg) in CH_2Cl_2 (0.5 mL) under argon was stirred for 2 h at room temperature. A solution of 3-(2-propenoyl)-2-oxazolidinone (15.5 mg, 0.11 mmol) in CH_2Cl_2 (1.0 mL) was added, and the reaction mixture was stirred 5 min at room temperature. The reaction mixture was cooled to −78 °C, and cyclopentadiene (50 μL, 0.59 mmol) was added. Once the starting material was consumed (40 h), the reaction was diluted with 2 mL of 1:1 EtOAc/*n*-hexane and filtered through a path of silica gel, and the filtrate was concentrated to dryness. The residue was purified by flash chromatography (*n*-hexane/EtOAc, 2:1) to afford a 98:2 mixture of endo/exo aducts [20.4 mg, 90% yield, 95% ee endo-(*R*)]. HPLC:[27] Diacel Chiralcel OD, *n*-hexane/*i*-PrOH, 90:10, flow rate 1.0 mL/min, exo t_R = 16.9, 17.6 min, endo-(*R*) t_R = 18.7 min, endo-(*S*) t_R = 20.8 min, 210 nm. Endo aduct:[27] ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.25 (dd, J = 3.0, 5.7 Hz, 1H), 5.88 (dd, J = 2.8, 5.7 Hz, 1H), 4.50−4.30 (m, 2H), 4.05−3.85 (m, 3H), 3.30 (s, 1H), 2.92 (s, 1H), 1.95 (ddd, J = 11.7, 9.2, 3.7 Hz, 1H), 1.55−1.35 (m, 3H). The same experimental procedure starting from [**1f**·CuBr]$_2$ (7.1 mg, 0.0056 mmol) and $AgBF_4$ (2.1 mg, 0.011 mmol) provided a 99:1 mixture of endo/exo aducts [19.7 mg, 87% yield, 54% ee endo-(*S*)].

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Supporting Information Available: Physical and spectral data for complexes (**1a**−**e**)·$PdCl_2$, **2**·$PdCl_2$, and [**1f**·CuCl]$_2$. Tables of atomic coordinates, thermal parameters, all bond distances and angles, and experimental data for X-ray diffraction studies of **1a**·$PtCl_2$ and **1e**·$PdCl_2$. Copies of ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0493762

(27) For HPLC and spectroscopic data of adducts (*R*)-**3** and (*S*)-**3**, see for instance: Evans, D. A.; Miller, S. J.; Lectka, T.; von Matt, P. *J. Am. Chem. Soc.* **1999**, *121*, 7559.