Palladium(0)-Catalyzed Cis−Trans Alkene Isomerizations

Luciano Canovese, Claudio Santo, and Fabiano Visentin*

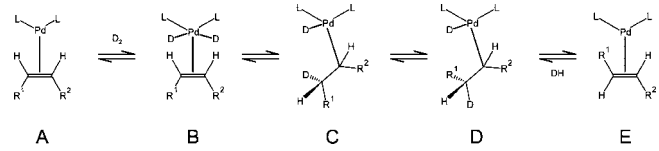
Dipartimento di Chimica, Università Ca′ Foscari, Calle Larga S. Marta 2137, 30123 Venezia, Italy

Received April 4, 2008

The cis−trans isomerization of some olefins bearing strong electron-withdrawing substituents (dmma and *E*-tse) is catalyzed by their mere coordination to a suitable Pd(0) fragment without any external reagents. The choice of spectator ligand is fundamental to the efficiency of the process, and the phosphanylquinolines dppq and dppq-Me have proven to be particularly effective. The mechanism of the rearrangement is discussed, and the presence of electron-withdrawing and conjugated substituents on the olefins appears to be an essential prerequisite for the isomerization.

The amazing number of research articles related to the cis−trans isomerization of olefins reflects the great importance of such a process in organic[1] and inorganic chemistry[2] as well as in biology.[3] In general (*Z*)- and (*E*)-olefins do not interconvert spontaneously at room temperature in the absence of an appropriate external promoter. The fundamental role of this agent is to support the formal breaking of the double bond via either a homolytic or a heterolytic process with consequent reduction in the energy barrier to rotation. The homolytic breaking of the π system has been basically observed in the case of direct photoisomerization,[3,4] of isomerization initiated by radical generators or paramagnetic molecules (atomic bromine or iodine, oxygen, nitrogen oxide, etc.),[5] and of electrochemical[6] or thermal isomerization.[7] The heterolytic breaking involves a reactive nucleophilic[8] or electrophlic[1b] counterpart, and the rupture of the double bond is greatly favored in an ethylene system where there are electron-withdrawing groups bound to one carbon and electron-donating substituents on the other. In this respect, groups conjugated to the double bond are particularly functional.

Scheme 1



Geometric olefin isomerizations may also be obtained by resorting to transition-metal assistance. Thus, it is noteworthy that many tungsten- or molybdenum-based catalysts exhibit a high efficiency both in metathesis and in isomerization of internal acyclic olefins as a consequence of the so-called "metal-alkylidene chain" mechanism.[9a–c] An efficient isomerization of *cis*-alkenes can also be achieved by Pd(II) catalysts, via a mechanism involving a carbocation.[9e] On the other hand, an extensive olefin isomerization is observed during the reduction of cis-alkenes or semihydrogenation of alkynes under dihydrogen atmosphere. Pd^0,[10] Ni^0,[11] Rh^I,[10,12] and Ir^I [13] catalysts are typically employed, and the mechanism seems to proceed via an equilibrium between a metal dihydrido olefin complex and a metal monohydrido alkyl complex.

In particular, Spencer and co-workers[10c] have found that during the palladium-catalyzed reduction of *cis*-olefins with deuterium, some *trans*-alkenes containing one deuterium atom are obtained (Scheme 1). This proves that deuterium is directly involved in the isomerization; furthermore, the same authors have shown that polarization of the metal−hydrogen bond determines the site of attack (from **B** to **C**) at the most electronically favored end of the double bond. However, a question is left unanswered: previous works[14] had established that the production of *trans*-alkene via β-elimination (from **D** to **E**) occurs with cis geometry and consequently, according to

* To whom correspondence should be addressed. E-mail: fvise@unive.it.

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10.1021/om800305h CCC: $40.75
Publication on Web 06/17/2008

Scheme 2

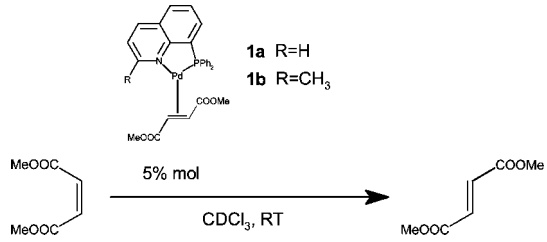


Table 1[a]

entry	cat. (amt (mol %))	*t* (h)	conversn (%)
1	**1b** (5)	6	56
2	**1b** (5)	24	95
3	**1b** (5)	48	99
4	**1a** (5)	6	56
5	**1a** (5)	24	86
6	**1a** (5)	48	97
6	**1b** (1)	24	28
7	**1b** (1)	48	43

[a] All reactions were run using the substrate dmfu at a concentration of 0.3 mol/dm^{-3}, in 0.8 mL of $CDCl_3$ at 298 K under an argon atmosphere.

Scheme 1, it would lead to 100% incorporation of deuterium into the final olefins. The experimental level of incorporated deuterium is not complete, and so, a competing mechanism may be possible. The simplest option is to assume that the metal adds first to the double bond of the *cis*-alkene and then isomerization could occur without the mediation of deuterium (directly from **A** to **E**).

Results and Discussion

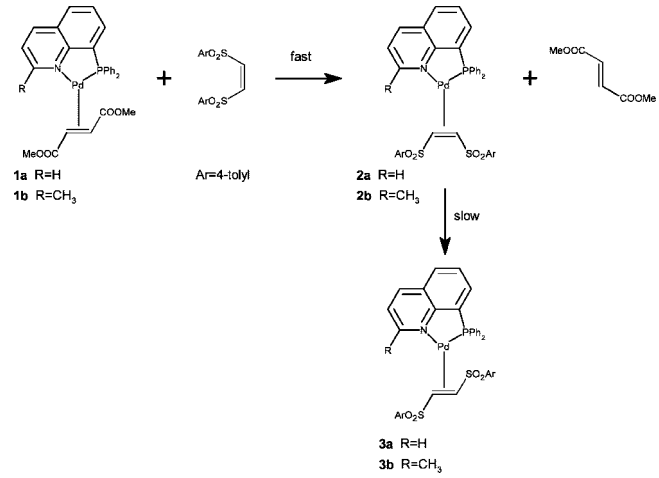
In the present paper we report a direct and exhaustive proof of an olefin isomerization mechanism promoted by a palladium(0) substrate without any other external mediation.

Our first observation involved the ability of the novel zerovalent palladium complexes [Pd(dppq)(η^2-dmfu)] (**1a**) and [Pd(dppq-Me)(η^2-dmfu)] (**1b**) (dmfu = dimethyl fumarate; dppq = 8-(diphenylphosphino)quinoline; dppq-Me = 8-(diphenylphosphino)-2-methylquinoline) to promote the complete isomerization of dimethyl maleate to its respective trans species dimethyl fumarate (Scheme 2). This catalytic transformation could be obtained in a $CDCl_3$ solution at room temperature (Table 1).

The simplest hypothesis of the mechanism for this catalysis entails a fast equilibrium displacement of the coordinated dimethyl fumarate by excess of dimethyl maleate to yield [Pd(dppq)(η^2-dmma)] (dmma = dimethyl maleate), followed by the slow cis−trans isomerization of the coordinated olefin. This suggestion is directly supported by the appearance of a small peak in the $^{31}P\{^1H\}$ NMR spectrum of the catalytic mixture after the addition of dimetyl maleate. This peak, with a chemical shift very near to that belonging to the catalytic species [Pd(dppq)(η^2-dmfu)], may be attributed to the complex [Pd(dppq)(η^2-dmma)]. The strong difference in intensity between the two peaks suggests that the displacement equilibrium is definitely favorable to **1a**. The minor peak consistently disappears at the end of the reaction when all dimethyl maleate has been converted into dimethyl fumarate.

The fundamental importance of the phosphanyl-quinoline ancillary ligands was immediately evident: the corresponding complexes [Pd(dppe)(η^2-dmfu)][15] (**1c**; dppe = 1,2-bis(diphenylphosphine)ethane), [Pd(neoc)(η^2-dmfu)][16] (**1d**; neoc = 2,9-dimethyl-1,10-phenanthroline), and [Pd(NSPh)(η^2-dmfu)][15] (**1e**; NSPh = 2-(phenylthiomethyl)pyridine) were virtually ineffective under the same mild operating conditions.

Scheme 3



These findings led us to verify the applicability of this catalytic system to other olefinic substrates. Our attention was therefore focused on the disulfonic derivative *Z*-tse (*Z*-tse = (*Z*)-1,2-bis[(4-methylphenyl)sulfonyl]ethene),[17] which electronically resembles dmfu. When a 3-fold excess of this olefin was added to complexes **1a**,**b** in $CDCl_3$, we could observe the immediate and complete displacement of dimethyl fumarate to produce respectively the new complexes **2a**,**b**; this result clearly showed the better efficiency of *Z*-tse in stabilizing the palladium(0) substrate.[18] Also in this case the complexes **2a**,**b** slowly turned into **3a**,**b** (∼12 h) through the cis−trans isomerization of coordinated olefin (Scheme 3). Interestingly, the excess *Z*-tse continued its conversion to *E*-tse[17] even after the complete formation of complexes **3a**,**b**, which thus displayed catalytic properties. Once again the course of the reactions could be easily deduced by the changes detected in the ^1H and $^{31}P\{^1H\}$

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(18) The complete displacement of dmfu by Z-tse is attested by determination of the equilibrium constant K_{E3}:

$$[\text{Pd(dppq)}(\eta^2\text{-dmfu})] + \text{Z-tse} \overset{K_{E3}}{\longleftrightarrow} [\text{Pd(dppq)}(\eta^2\text{-Z-tse})] + \text{dmfu}$$

Its value was not directly accessible, as it was too high, but it could be indirectly estimated by spectrophotometric determinations of the olefin substitution equilibrium constants K_{E1} and K_{E2} concerning the reactions:

$$[\text{Pd(dppq)}(\eta^2\text{-dmfu})] + \text{fn} \overset{K_{E1}}{\longleftrightarrow} [\text{Pd(dppq)}(\eta^2\text{-fn})] + \text{dmfu}$$

$$[\text{Pd(dppq)}(\eta^2\text{-fn})] + \text{Z-tse} \overset{K_{E2}}{\longleftrightarrow} [\text{Pd(dppq)}(\eta^2\text{-Z-tse})] + \text{fn}$$

with dmfu = dimethyl fumarate and fn = fumaronitrile. The values obtained were K_{E1}= 4600 ± 600 and K_{E2} = 270 ± 50. From these findings the value of K_{E3}, given by the product of K_{E1} and K_{E2}, was (1.2 ± 0.3) × 10^6. For a detailed description of the method see the Supporting Information and: Canovese, L.; Visentin, F.; Uguagliati, P.; Crociani, B. *J. Chem. Soc., Dalton Trans.* **1996**, 1921–1926.

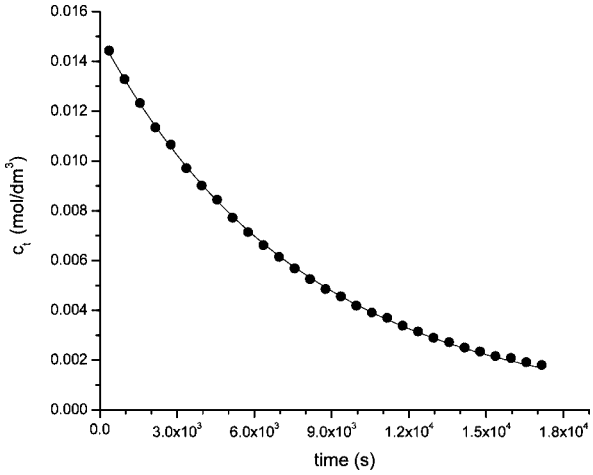


Figure 1. Fit of concentration of starting complex **2b** to time according to eq 1 in $CDCl_3$ at 25 °C ($c_0 = 1.5 \times 10^{-2}$ mol dm^{-3}).

NMR spectra. It is noteworthy that this system offers the feasibility to isolate the intermediates complexes **2a**,**b** with the coordinated olefin in a cis arrangement; their precipitates could be simply obtained by treating with diethyl ether a CH_2Cl_2 solution of starting compounds **1a**,**b** kept at low temperature (−15 °C) immediately after the addition of *Z*-tse. In contrast, a long reaction time (several hours at room temperature) ensured the complete conversion of **2a**,**b** into the thermodynamically more stable species **3a**,**b**.[19]

Both of these products were isolated as yellow crystalline solids, which are stable at room temperature for months in a closed vessel without any tendency of the cis species to turn into the corresponding trans isomer. The elemental analyses of **2a**,**b** were the same as those of **3a**,**b**, respectively, and resulted in good agreement with the expected composition. In contrast, the ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra revealed some appreciable differences which allowed us to distinguish easily the cis from the trans products.

All these circumstances represented very favorable conditions for a kinetic study focused on the isomerization process. Indeed, in $CDCl_3$ solution at 298 K the complexes **2a**,**b** rearranged at a rate for which monitoring by NMR spectroscopy is feasible. In particular, for the species **2b** a set of concentration vs time data could be obtained with high precision from relevant signals of ^{1}H NMR spectra (Figure 1). In this case we could observe that the consumption of starting material followed a first-order rate law according to eq 1.

$$c_t = c_0 \exp(-k_1 t) \qquad (1)$$

The analysis yielded the rate constant $k_1 = (1.27 \pm 0.01) \times 10^{-4}$ s^{-1}.

This kinetic evidence supports strongly our hypothesis of a unimolecular rearrangement for the coordinated olefin isomerization.

The strategic role of phosphanyl-quinoline ligands in this process is once again highlighted by comparison with the behavior of analogous palladium(0) complexes **1c**−**e** bearing different ancillary ligands. As a matter of fact, after their treatment with an equimolar amount of *Z*-tse we could observe

(19) The complexes **3a**,**b** could also be obtained by direct exchange of dmfu in the starting compounds **1a**,**b** with *E*-tse (*E*-tse = (*E*)-1,2-bis[(4-methylphenyl)sulfonyl]ethane). This olefin was synthesized according to the procedure described in ref 17.

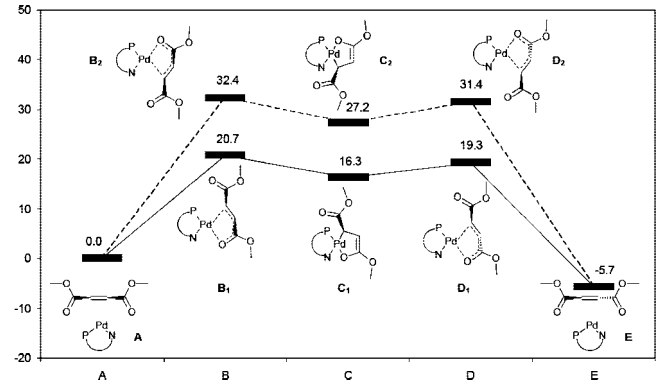
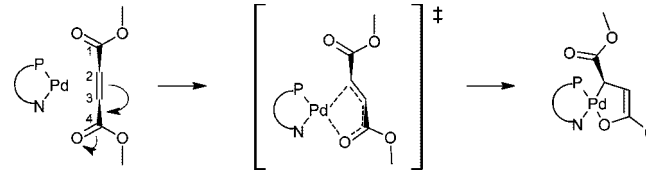


Figure 2. Gibbs free energy values (kcal/mol) for the different reaction paths computed at the B3PW91 level.

Scheme 4



again the complete replacement of dimethyl fumarate by the more effective olefin added, with the consequent formation of the new species **2c**−**e**, but no or only a weak tendency to the subsequent cis−trans isomerization of the coordinated olefin. In particular, the complexes **2d**,**e** (with neoc and NSPh as ancillary ligands, respectively), were substantially unreactive, while the conversion of the diphosphino complex **2c** into the species **3c** containing *E*-tse required some weeks.

In light of the above findings it is reasonable to suppose that the promotion of this unprecedented olefin rearrangement must fundamentally stems from a cooperative and subtle influence of the two coordinating groups of the spectator ligand on the Pd−alkene bond. In an attempt to gain information concerning this point, the reaction mechanism was investigated employing density functional theory (DFT) calculations. The simulated system concerned the isomerization of the complex [Pd(dmpq)(η^2-dmma)] (dmpq = 8-(dimethylphosphino)quinoline) into the corresponding [Pd(dmpq)(η^2-dmfu)]. Replacing the two phenyl phosphorus substituents of the experimentally tested dppq ligand with two methyl groups makes the process less computationally intensive.

Schematic energy profiles (ΔG values) are shown in Figure 2.

It is apparent that the reaction can proceed following two similar but distinct pathways.

For both pathways we detected a high-energy Pd^{II}-cyclometalated intermediate (**C$_1$** or **C$_2$**), produced by a sort of nucleophilic attack of the electron-rich palladium(0) fragment to the α,β-unsaturated coordinated olefin. The addition was conjugate (1,4) with consequent formation of two new Pd−C and Pd−O σ bonds and the shift of the olefinic double bond from the 2,3- to the 3,4-position (Scheme 4).

Both intermediates were connected to the reactants and to the products by two transition states (**B$_1$** or **B$_2$** and **D$_1$** or **D$_2$**) in which the olefinic double bond is partially twisted and elongated and the carbonyl oxygen is partially bonded to palladium. Pathway 1 was significantly favored by the low energy profile, determined by the strong trans effect/influence of the phosphorus which weakens the Pd−C(3) bond in the starting complex **A**, and by the higher stability of the intermediate **C$_1$** which has phosphorus and carbon in cis and not in trans reciprocal

positions (as for the $\mathbf{C_2}$ species). The activation energy of the low-energy path (20.7 kcal/mol) is quite compatible with our experimental findings.

Eventually these results explained the decisive and peculiar role of phosphanyl-quinoline in promoting the olefin rearrangement: on one side the presence of the strong trans-labilizing phosphine group favors activation of the initial compound, and on the other the weak trans-labilizing quinoline group provides sufficient stability to the key intermediate $\mathbf{C_1}$. Moreover, the calculations emphasized the crucial role exercised by the conjugate C═O group for the outcome of the whole process. This evidence seems to reduce significantly the spectrum of olefins fit for this mechanism of rearrangement. Among the functional groups able to perform the same role of carbonyl, we could experimentally verify the appreciable ability of the sulfonyl unit.

In conclusion, we have shown both experimentally and theoretically an original mechanism for the cis−trans isomerization of alkenes promoted exclusively by a palladium(0) fragment. Further work is currently under way to define precisely the range of substituents on the olefin and the range of ancillary ligands of palladium(0) complexes required to ensure good efficiency to the process.

Experimental Section

Materials. Unless otherwise stated, all manipulations were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were purified by standard procedures and distilled under argon immediately prior to use.

dppq,[20] dppq-Me,[20] $Pd_2DBA_3\cdot CHCl_3$,[21] [Pd(dppe)(η^2-dmfu)][15] (**1c**), [Pd(neoc)(η^2-dmfu)][16] (**1d**), and [Pd(NSPh)(η^2-dmfu)][15] (**1e**) were prepared by following literature procedures. All other chemicals were commercial grade and were used without further purification.

1D and 2D NMR spectra were recorded using a Bruker DPX300 or Bruker DPX500 spectrometer. Chemical shifts (ppm) are given relative to TMS (^{1}H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR). Peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). The proton and carbon assignment was performed by ^{1}H-2D COSY, ^{1}H 2D NOESY, ^{1}H−^{13}C HMQC, and HMBC experiments.

Synthesis of [Pd(dppq)(η^2-dmfu)] (1a) and [Pd(dppq-Me)(η^2-dmfu)] (1b). To a solution of dmfu (0.0640 g, 0.44 mmol) and the appropriate bidentate ligands (0.405 mmol) in dry acetone (15 mL) was added solid $Pd_2DBA_3\cdot CHCl_3$ (0.200 g, 0.193 mmol) under an inert atmosphere (argon). The reaction mixture was stirred for 1 h at room temperature, and the initial dark suspension turned to an orange-yellow solution. This resulting solution was dried under reduced pressure, and the residue was redissolved in dichloromethane. Addition of charcoal and filtration on Celite removed the traces of metallic palladium, yielding a clear solution. Reduction to small volume (3−4 mL) and addition of diethyl ether gave the products as microcrystalline yellow solids after cooling to 0 °C (0.1764 g, yield 80.1% for **1a**; 0.1802 g, yield 80.7% for **1b**).

Selected data for **1a**: ^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ 3.37 (s, 3H, OCH_3 trans-P), 3.70 (s, 3H, OCH_3 trans-N), 4.11 (t, 1H, $J_{CH=CH}$ = 10.5 Hz, J_{PH} = 10.5 Hz, CH═CH trans-P), 4.52 (dd, 1H, $J_{CH=CH}$ = 9.2 Hz, J_{PH} = 2.2 Hz, CH═CH trans-N), 7.33−7.48 (m, 8H, PPh_2), 7.56 (dd; H, J = 8.3 Hz; J = 4.7 Hz, H^3), 7.63−7.70 (m, 2H, PPh_2, H^6), 7.96−8.01 (m, 2H, H^5, H^7), 8.37 (d, 1H, J = 8.3 Hz, H^4), 9.43 (d, 1H, J = 4.7 Hz, H^2); ^{31}P{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ 20.8; ^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ 48.8 (CH_3, OCH_3, trans-P); 49.5 (d, CH, J_{CP} = 28.6 Hz, CH═CH trans-P), 50.5 (CH_3, OCH_3, trans-N), 50.7 (CH, CH═CH trans-N), 122.8 (CH, C^3), 127.3 (d, CH, J_{CP} = 4.3 Hz, C^6), 130.7 (CH, C^5), 136.6 (d, C, J_{CP} = 31.3 Hz, C^8), 137.7 (d, CH, J_{CP} = 2.5 Hz, C^7), 137.9 (CH, C^4), 151.1 (C, C^9), 151.4 (C, C^{10}), 155.4 (CH, C^2), 173.0 (d, CO, J_{CP} = 5.8 Hz, CO trans-N), 174.3 (CO, CO trans-P); IR (KBr pellet) ν 1632 cm^{-1} (C═O). Anal. Calcd for $C_{27}H_{24}NO_4PPd$: C, 57.51; H, 4.29; N, 2.48. Found: C, 57.65; H, 4.39; N, 2.44.

Selected data for **1b**: ^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ 3.16 (s, 3H, quinoline-CH_3); 3.21 (s, 3H, OCH_3 trans-P), 3.64 (s, 3H, OCH_3 trans-N), 3.96 (t, 1H, $J_{CH=CH}$ = 10.5 Hz, J_{PH} = 10.5 Hz, CH═CH trans-P); 4.50 (dd, 1H, $J_{CH=CH}$ = 9.2 Hz, J_{PH} = 2.4 Hz, CH═CH trans-N), 7.31−7.45 (m, 8H, PPh_2), 7.56 (d, H, J = 8.4 Hz; H^3), 7.58 (t, 1H, J = 7.7 Hz, H^6), 7.70−7.76 (m, 2H, PPh_2), 7.85 (t, 1H, J_{HH} = J_{HP} = 7.7 Hz, H^7), 7.92 (d, H, J = 7.7 Hz, H^5), 8.21 (d, 1H, J = 8.4 Hz, H^4); ^{31}P{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ 20.6; ^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ 31.8 (CH_3, quinoline-CH_3), 48.1 (d, CH, J_{CP} = 31.8 Hz, CH═CH trans-P), 49.1 (CH, CH═CH *trans*-N), 50.4 (CH_3, OCH_3, trans-P), 50.5 (CH_3, OCH_3, trans-N), 123.3 (CH, C^3), 126.1 (d, CH, J_{CP} = 4.4 Hz, C^6), 130.7 (CH, C^5), 135.2 (d, C, J_{CP} = 31.3 Hz, C^8), 137.5 (CH, C^7), 138.1 (CH, C^4), 151.5 (C, C^9), 151.8 (C, C^{10}), 164.0 (C, C^2), 174.0 (CO, CO trans-P), 174.3 (d, CO, J_{CP} = 5.5 Hz, CO trans-N); IR (KBr pellet) ν 1697, 1677 cm^{-1} (C═O). Anal. Calcd for $C_{28}H_{26}NO_4PPd$: C, 58.19; H, 4.53; N, 2.42. Found: C, 58.36; H, 4.64; N, 2.39.

Synthesis of Complexes 2a,b. A solution of complex **1a** or **1b** (0.2 mmol) in dry dichloromethane was cooled to −15 °C, and solid *Z*-tse (0.0673 g, 0.2 mmol) was quickly added under an inert atmosphere (argon). The reaction mixture was stirred for 5 min and then dried under reduced pressure. The pale yellow solid obtained was washed with several aliquots of diethyl ether to remove the free dmfu (0.1295 g, yield 92.3% for **2a**; 0.1358 g, yield 88.2% for **2b**). Analytically pure complexes were obtained by recrystallization from CH_2Cl_2/Et_2O.

Selected data for **2a**: ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ 2.32 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.95 (dd, 1H, $J_{CH=CH}$ = 9.3 Hz, J_{PH} = 8.0 Hz, CH═CH trans-P), 4.24 (dd, 1H, $J_{CH=CH}$ = 9.3 Hz, J_{PH} = 2.5 Hz, CH═CH trans-N); 6.91 (d, 2H, J = 8.1 Hz, H^c), 7.15 (d; 2H, J = 8.1 Hz, H^c), 7.29−7.46 (m, 10H, PPh_2, H^b), 7.64 (dd, 1H, J = 8.3 and 4.8 Hz, H^3), 7.7 (dd, 1H, J = 8.0 Hz, J_{PH} = 8.0, H^7), 7.83−7.92 (m, 4H, PPh_2), 7.96 (t, 1H, J = 8.0 Hz, H^6), 8.02 (d, 1H, J = 8.0 Hz, H^5), 8.40 (d, 1H, J = 8.3 Hz, H^4), 10.28 (d, 1H, 4.8 Hz, H^2); ^{31}P{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ 22.7; IR (KBr pellet) ν 1297, 1128 cm^{-1} (S═O). Anal. Calcd for $C_{37}H_{32}NO_4PPdS_2$: C, 58.77; H, 4.27; N, 1.85. Found: C, 58.65; H, 4.22; N, 1.82.

Selected data for **2b**: ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ 2.08 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.32 (s, 3H, CH_3 quinoline), 4.13 (dd, 1H, $J_{CH=CH}$ = 9.3 Hz, J_{PH} = 8.0 Hz, CH═CH trans-P), 4.22 (dd, 1H, $J_{CH=CH}$ = 9.3 Hz, J_{PH} = 2.5 Hz, CH═CH trans-N), 6.77 (d, 2H, J = 7.9 Hz, H^c), 7.08 (d, 2H, J = 7.9 Hz, H^c), 7.34−7.63 (m, 15H, PPh_2, H^7, H^3, H^6, H^b), 7.90 (d, 2H, J = 7.9 Hz, H^b), 7.96 (d, 1H, J = 7.9 Hz, H^5), 8.26 (d, 1H, J = 8.5 Hz, H^4); ^{31}P{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ 24.9; IR (KBr pellet) ν 1298, 1128 cm^{-1} (S═O). Anal. Calcd for $C_{37}H_{32}NO_4PPdS_2$: C, 58.77; H, 4.27; N, 1.85. Found: C, 58.62; H, 4.18; N, 1.82.

Synthesis of Complexes 3a,b. To a solution of complex **1a** or **1b** (0.2 mmol) in dry dichloromethane was added solid *Z*-tse (0.0673 g, 0.2 mmol) under an inert atmosphere (argon). The reaction mixture was stirred for 24 h, treated with activated charcoal, and filtered off on a Celite layer. The clear solution was concentrated to a small volume under reduced pressure and diluted with

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diethyl ether to precipitate the title products as cream-colored microcrystals (0.1240 g, yield 82.0% for **3a**; 0.1215 g, yield 78.9% for **3b**).

Selected data for **3a**: ^{1}H NMR ($CDCl_3$, $T = 298$ K, ppm) δ 2.37 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 4.18 (dd, 1H, $J_{CH=CH} = 9.2$ Hz, $J_{PH} = 9.2$ Hz, CH=CH trans-P); 4.65 (dd, 1H, $J_{CH=CH} = 9.2$ Hz, $J_{PH} = 1.6$ Hz, CH=CH trans-N), 6.94 (d, 2H, $J = 8.6$ Hz, H^c), 6.97 (d, 2H, $J = 8.6$ Hz, H^c), 7.39−7.44 (m, 10H, PPh_2, H^b), 7.64 (dd, 1H, $J = 8.6$ and 4.6 Hz, H^3), 7.68−7.84 (m, 5H, PPh_2, H^7), 8.00−8.04 (m, 2H, H^5, H^6), 8.40 (d, 1H, $J = 8.6$ Hz, H^4), 10.22 (d, 1H, $J = 4.6$ Hz, H^2); ^{31}P{^{1}H} NMR ($CDCl_3$, $T = 298$ K, ppm) δ 23.7; ^{13}C{^{1}H} NMR ($CDCl_3$, $T = 298$ K, ppm) δ 21.4 (CH_3, $PhCH_3$, trans-P and trans-N), 60.5 (d, CH, $J_{CP} = 50.5$ Hz, CH=CH trans-P), 64.6 (CH, CH=CH trans-N), 123.1 (CH, C^3), 126.0 (CH, C^b), 126.6 (CH, C^b), 127.4 (d, CH, $J_{CP} = 4.3$ Hz, H^7), 129.0 (CH, C^c), 129.1 (CH, C^c), 131.1 (CH, C^5), 136.0 (d, C, $J_{CP} = 32.9$ Hz, C^8), 137.8 (CH, C^6), 138.2 (CH, C^4), 139.4 (C, C^a), 140.8 (C, C^a), 141.4 (C, C^d), 141.7 (C, C^d), 151.2 (C, C^{10}), 151.5 (C, C^9), 159.5 (CH, C^6); IR (KBr pellet) ν 1295, 1141 cm^{-1} (S=O). Anal. Calcd for $C_{37}H_{32}NO_4PPdS_2$: C, 58.77; H, 4.27; N, 1.85. Found: C, 58.88; H, 4.38; N, 1.88.

Selected data for **3b**: ^{1}H NMR ($CDCl_3$, $T = 298$ K, ppm) δ 2.36 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.42 (s, 3H, CH_3 quinoline), 4.13 (dd, 1H, $J_{CH=CH} = 9.1$ Hz, $J_{PH} = 9.1$ Hz, CH=CH trans-P), 4.50 (dd, 1H, $J_{CH=CH} = 9.2$ Hz, $J_{PH} = 2.3$ Hz, CH=CH trans-N), 6.91 (d, 2H, $J = 8.6$ Hz, H^c), 6.94 (d, 2H, $J = 8.6$ Hz, H^c), 7.37−7.47 (m, 10H, PPh_2, H^b), 7.57−7.79 (m, 7H, PPh_2, H^3, H^7, H^6), 7.96 (d, 1H, $J = 8.0$ Hz, H^5), 8.25 (d, 1H, $J = 8.5$ Hz, H^4); ^{31}P{^{1}H} NMR ($CDCl_3$, $T = 298$ K, ppm) δ 23.7; IR (KBr pellet) ν 1297, 1136 cm^{-1} (S=O). Anal. Calcd for $C_{37}H_{32}NO_4PPdS_2$: C, 58.77; H, 4.27; N, 1.85. Found: C, 58.94; H, 4.36; N, 1.89.

Synthesis of Complexes 2c−e. *Z*-tse (0.0673 g, 0.2 mmol) was added to a solution prepared by dissolving 0.2 mmol of complex **1c**[15] (or **1d**[16] or **1e**[15]) in dry dichloromethane (15 mL). The reaction mixture was stirred for 30 min and then evaporated to dryness in vacuo. The resulting white solids were carefully washed first with dry diethyl ether (3 × 5 mL) and then *n*-pentane (2 × 5 mL) (0.1635 g, yield 97.2% for **2c**; 0.1226 g, yield 94.2% for **2d**; 0.1190 g, yield 92.4% for **2e**).

Selected data for **2c**: ^{1}H NMR ($CDCl_3$, $T = 298$ K, ppm) δ 2.12−2.59 (m, 4H, CH_2P), 2.33 (s, 3H, CH_3), 4.20 (m, AA′XX′ system, CH=CH, 2H), 6.96 (d, 4H, $J = 8.1$ Hz, H^c), 7.40 (m, H^o and H^p, 12H), 7.55 (d, 4H, $J = 8.2$ Hz, H^b), 7.84 (m, H^m, 8H); ^{31}P{^{1}H} NMR ($CDCl_3$, $T = 298$ K, ppm) δ 41.8; ^{13}C{^{1}H} NMR ($CDCl_3$, $T = 298$ K, ppm) δ 21.4 (CH_3, $PhCH_3$), 27.5 (m, AXX′ system, CH_2, CH_2P), 65.8 (d, CH, $J_{CP} = 45.7$ Hz, CH=CH), 126.8 (CH, C^b), 129.7 (CH, C^c), 141.4 (C, C^a), 141.5 (C, C^d); IR (KBr pellet) ν 1292, 1138 cm^{-1} (S=O). Anal. Calcd for $C_{42}H_{40}O_4P_2PdS_2$: C, 59.96; H, 4.79%. Found: C, 59.80; H, 4.74.

Selected data for **2d**: ^{1}H NMR ($CDCl_3$, $T = 298$ K, ppm): δ 2.30 (s, 6H, Ph*CH*$_3$), 3.25 (s, 6H, neoc-CH_3), 4.31 (s, 2H, CH=CH), 6.96 (d, 4H, $J = 8.1$ Hz, H^c), 7.60 (d, 2H, $J = 8.3$ Hz, H^3), 7.64 (d, 4H, $J = 8.1$ Hz, H^b), 7.81 (s, 2H, H^5), 8.23 (d, 2H, $J = 8.1$ Hz, H^4); ^{13}C{^{1}H} NMR ($CDCl_3$, $T = 298$ K, ppm) δ 21.4 (CH_3, $PhCH_3$), 29.9 (CH_3, neoc-CH_3), 55.2 (CH, CH=CH), 124.9 (CH, C^3), 125.5 (CH, C^5), 127.0 (CH, C^b), 127.2 (C, C^6), 128.4 (CH, C^c), 137.1 (C, $C^{4,7}$), 132.8 (CH, C^9), 138.0 (CH, C^4); 141.2 (C, C^a), 141.6 (C, C^d), 145.6 (C, C^7), 162.3 (C, C^2); IR (KBr pellet) ν 1286, 1131 cm^{-1} (S=O). Anal. Calcd for $C_{30}H_{28}N_2O_4PdS_2$: C, 55.34; H, 4.33; N, 4.30. Found: C, 55.22; H, 4.26; N, 4.39.

Selected data for **2e**: ^{1}H NMR ($CDCl_3$, $T = 298$ K, ppm) δ 2.29 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 4.01 (d, 1H, $J = 9.2$ Hz, CH=C, trans-N), 4.11 (d, 1H, $J = 9.2$ Hz, CH=CH, trans-S), 4.36, 4.42 (AB system, 2H, $J = 16.1$ Hz, CH_2S), 7.01 (d, 2H, $J = 8.1$ Hz, H^c), 7.23 (d, 2H, $J = 8.1$ Hz, H^c), 7.26−7.34 (m, 5H, H^3, H^5, H^{10}, H^8), 7.63−7.68 (m, 4H, H^b, H^9), 7.74 (d, 1H, $J = 7.7$ Hz, H^4), 7.94 (d, 2H, $J = 8.1$ Hz), 9.67 (d, 1H, $J = 4.4$ Hz, H^6); ^{13}C{^{1}H} NMR ($CDCl_3$, $T = 298$ K, ppm) δ 21.4 (CH_3, $PhCH_3$), 21.5 (CH_3, $PhCH_3$), 47.5 (CH_2, CH_2S), 60.6 (CH, CH=CH, trans-S), 61.5 (CH, CH=CH trans-N), 123.0 (CH, C^3), 124.1 (CH, C^5), 127.4 (CH, C^b), 127.5 (CH, C^b), 128.7 (CH, C^c), 129.0 (CH, C^c), 129.2 (CH, C^{10}), 129.3 (CH, C^8), 131.9 (C, C^7), 132.8 (CH, C^9), 138.0 (CH, C^4), 140.7 (C, C^a), 140.8 (C, C^a), 142.2 (C, C^d), 142.4 (C, C^d), 155.2 (CH, C^2), 156.9 (C, C^6); IR (KBr pellet) ν 1293, 1136 cm^{-1} (S=O). Anal. Calcd for: $C_{28}H_{27}NO_4PdS_3$: C, 52.21; H, 4.22; N, 2.17. Found: C, 52.27; H, 4.29; N, 2.26.

Computational Details. The calculations were performed with the Gaussian03 package[22] at the B3PW91 level[23] using Ahlrichs's def2-SVP[24] basis set. The geometry optimizations were performed without any symmetry constraint, followed by analytical frequency calculations to confirm that a minimum or a transition state had been reached. Cartesian coordinates and energies of stationary points are reported in the Supporting Information.

Acknowledgment. We thank Profs. O. De Lucchi, F. Fabris, and S. Cossu for helpful suggestions about the synthesis of sulfones.

Supporting Information Available: Tables giving Cartesian coordinates and energies of stationary points and figures giving nonlinear regression fits. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800305H

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