Synthesis and Insertion Reactions of the Cyclometalated Palladium−Alkyl Complexes Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)L$_2$. Observation of a Pentacoordinated Intermediate in the Insertion of SO$_2$

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Palladacycles of the type Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)L$_2$, **2**, have been synthesized by treatment of the corresponding chloroalkylcomplexes Pd(CH$_2$CMe$_2$C$_6$H$_5$)ClL$_2$ (L$_2$ = (PMe$_3$)$_2$, **2a**, or 1,5-cyclooctadiene (cod), **2b**) with suitable bases, or by simple ligand exchange reactions from the cyclooctadiene derivative **2b**. The metallacycles **2** react with activated alkynes and with sulfur dioxide, giving rise to different insertion products.

Introduction

The chemistry of group 10 metallacycles has experienced an important development in the past years due to the involvement of these compounds as intermediates in different types of catalytic reactions and to their numerous applications in organic synthesis.[1] Benzannelated complexes of the type M(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)L$_2$ (M = Ni,[2a,b] Pt[3]) stand among the best studied metallacycles of this group, due in part to their ready synthesis by thermal decomposition of the bis(neophyl) derivatives M(CH$_2$CMe$_2$C$_6$H$_5$)$_2$L$_2$. The rich insertion chemistry of the nickel compound Ni(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(PMe$_3$)$_2$ has been exploited in synthetically useful transformations, and its study has provided a good model for metallacyclic reactivity.[2] In addition, the mechanism of the formation of the corresponding platinum complexes is now well understood, on the basis of the detailed studies carried out by Young and co-workers.[3] Therefore, it is somewhat surprising that, despite the well-known ability of palladium complexes to undergo cyclometalation processes,[4] the corresponding palladium metallacycles Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)L$_2$ have been reported only recently in preliminary form.[5] In this paper we provide full details for the synthesis of this type of metallacycle, including the cyclooctadiene derivative Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(cod), **2b**, which is a useful starting material, that allows the introduction of a variety of co-ligands. Additionally, we describe their reactivity toward unsaturated molecules such as alkynes and SO$_2$.

Results and Discussion

Synthesis of the Palladacycles Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)L$_2$. The nickel and platinum bis(neophyl) complexes M(CH$_2$-

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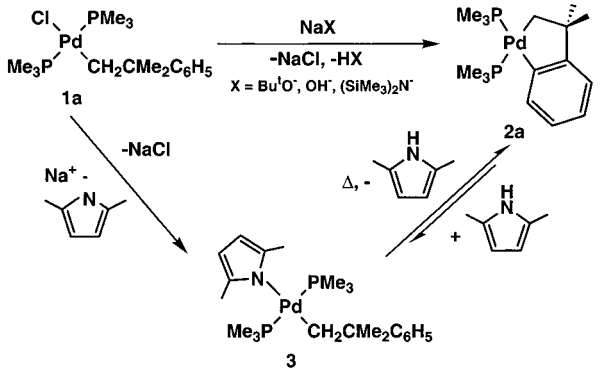
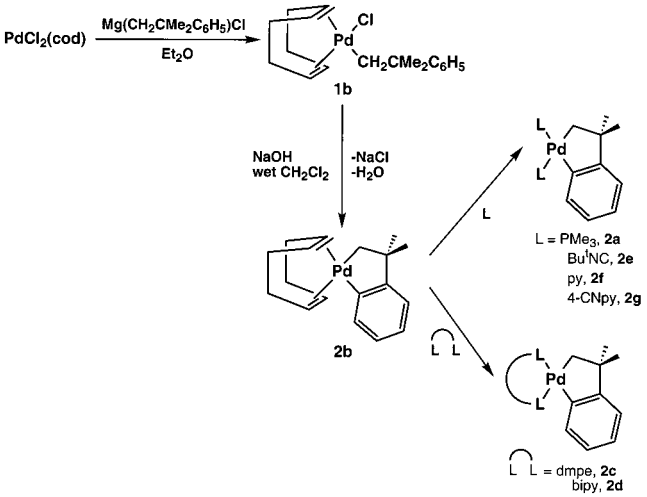
Scheme 1



$CMe_2C_6H_5)_2(PR_3)_2$[2a,b,3] experience a thermal, intramolecular cyclometalation that allows the efficient synthesis of the corresponding metallacycles $M(CH_2CMe_2\text{-}o\text{-}C_6H_4)(PMe_3)_2$. For palladium, however, this procedure is thwarted by the ready decomposition of the corresponding dialkyls.[6a] For example, the trimethylphosphine derivative $Pd(CH_2CMe_2C_6H_5)_2(PMe_3)_2$[6b,c] undergoes clean reductive elimination of 2,4-dimethyl-2,4-diphenylhexane (bineophyl) when heated in solution at 50 °C (see Experimental Section). Since closely related palladium metallacycles of composition $Pd(CH_2X\text{-}o\text{-}C_6H_4)L_2$ (X = O, NR; L = P- or N-donor) are stable species, readily synthesized by an intramolecular transmetalation reaction,[7] it appears likely that our target compound $Pd(CH_2CMe_2\text{-}o\text{-}C_6H_4)(PMe_3)_2$, **2a**, could form under the appropriate experimental conditions. Early work by Catellani and Chiusoli,[8a−c] subsequently followed by others,[8d] has demonstrated that (halo)alkyl complexes of palladium that possess a β−phenyl group can be cyclometalated by bases, much in the same fashion as the well-known cyclopalladation of aromatic amines, imines, and other nitrogen ligands.[4] Using a similar approach, we have prepared the desired metallacycle, **2a**, by treatment of the chloroneophyl complex **1a** with suitable bases (Scheme 1).[5]

The selection of the base is important to achieve a clean conversion of **1a** to **2a**. Sodium bis(trimethylsilyl)amide has proved to be particularly efficient, but other reagents such as sodium hydroxide, or alkali metal alkoxides and amides, can also effect the cyclometalation (albeit in lower yields or less cleanly). The sensitivity of this process to the nature of the basic reagent might be due to the ability of the latter to displace the chloro ligand from **1a**, giving rise to intermediate complexes that cyclometalate slowly or incompletely, or find other decomposition pathways in competition with the cyclometalation. For instance, the reaction of **1a** with 2,5-dimethylpirrolylsodium leads to the substitution product **3** (Scheme 1),

Scheme 2



which, although stable at room temperature, eliminates reversibly 2,5-dimethylpyrrole when heated at 50 °C in CD_2Cl_2, leading to an equilibrium mixture of **2a** and **3** ($K_{eq} \approx 0.52$ at this temperature). The same equilibrium mixture can be reached if solutions that contain equimolar amounts of **2a** and 2,5-dimethylpyrrole are heated at 50 °C. These observations suggest that the cyclometalation of **1a** is induced more effectively by bases with a low capacity to coordinate to the Pd center. It is worth noting that at variance with the above results, the reaction of the nickel analogue of **1a** with sodium hydroxide or 2,5-dimethylpyrrolylsodium leads to stable hydroxo and pyrrolyl complexes that do not undergo the cyclometalation reaction.[9]

The results described above show that the conditions required to effect the cyclometalation of a neophyl ligand in Pd complexes differ significantly from those needed for the similar Ni or Pt derivatives. For the latter metals the cyclometalation is accomplished by electron-rich bis(neophyl)complexes, whereas in the Pd system, the activation of the C−H bond appears to involve a cationic intermediate,[5] thereby suggesting an electrophilic attack of the Pd atom on the aromatic ring.

With the purpose of improving the synthesis of palladium metallacycles of type **2**, we have studied the cyclometalation of the neophyl complex **1b**, containing the 1,5-cyclooctadiene ligand (cod). This compound is the synthetic precursor of **1a** and is readily available from $PdCl_2(cod)$. Moreover, since cod is much poorer a donor than PMe_3, the enhanced electrophilicity of the Pd center in **1a** should facilitate the cyclometalation process. In accord with these expectations **2b** is readily formed when a solution of **1b** in moist THF or CH_2Cl_2 is treated with grounded sodium hydroxide (Scheme 2). Further elaboration of this synthetic methodology allows the direct preparation of **2b** (without isolation of **1b**) in 70−80% yield, based on $PdCl_2(cod)$ (see Experimental Section), as well as the generation of the related palladacycles **2a**−**2g** (vide infra).

Compounds **2a** and **2b** are very stable and can be handled in air without apparent decomposition. Their structures, first established on the basis of spectroscopic and analytical data, have been confirmed by X-ray diffraction studies (see Figures 1 and 2) to be discussed in a later section.

Alkylpalladium complexes with labile co-ligands are of interest because they permit tuning the electronic or the steric

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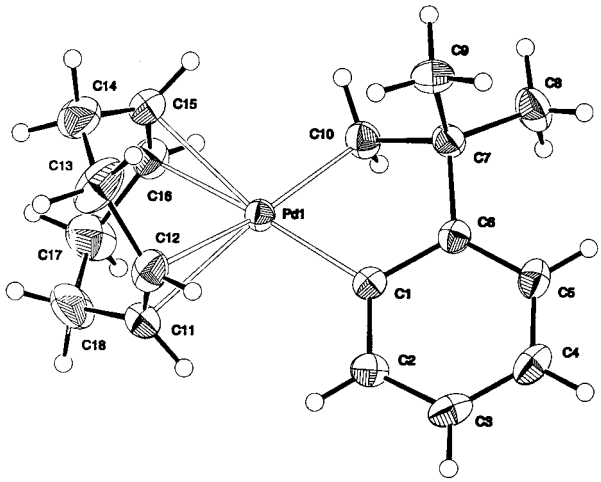

Figure 1. X-ray structure of complex **2b**.

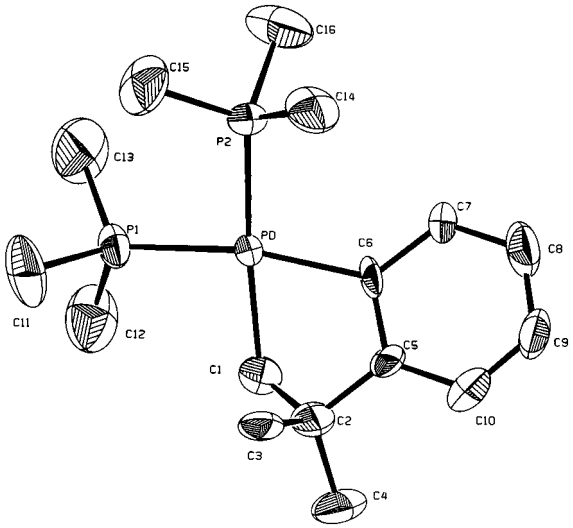

Figure 2. X-ray structure of complex **2a**.

environment of the metal center by simple ligand exchange reactions.[10] As already mentioned, the ready availability of **2b** and its easy manipulation makes this complex an excellent starting material for the preparation of a wide range of palladium metallacyclic derivatives (Scheme 2). Thus, on a preparative scale, **2a** is best obtained by treating **2b** with 2 equiv of PMe_3. Similar exchange reactions occur with *t*-butylisocyanide, 1,2-bis(dimethyphosphino)ethane (dmpe), or 2,2′-bipyridyl. Derivatives of pyridine (**2f**) and even of the less basic ligand 4-cyanopyridine (**2g**) can also be generated, but the bulkier α,α′-lutidine fails to displace the cyclooctadiene from **2b**.

NMR spectra of analytically pure samples of the pyridine (**2f**) and 4-cyanopyridyne complexes (**2g**) display sharp resonances, which nevertheless broaden readily in the presence of trace amounts of the free ligand or other impurities, indicating the occurrence of fast, associative ligand exchange processes. Similarly, the NMR spectra of **2a** reveal ligand exchange in the presence of added PMe_3. Figure 3 shows the effect of added PMe_3 on the room temperature $^{13}C\{^1H\}$ spectrum of **2a** (0.24 M in CD_2Cl_2). As can be seen, the exchange rate of the two PMe_3 ligands is appreciably different, this being evinced by the

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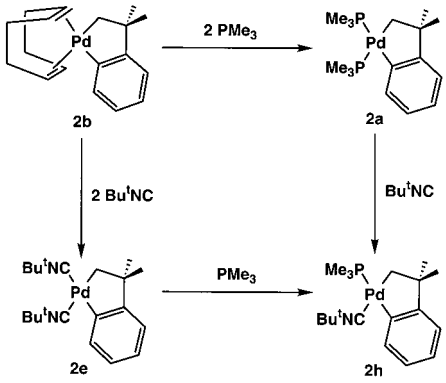
Scheme 3



selective broadening of only one of the two signals at low concentrations of the added trimethylphosphine (0.02 M, Figure 3b). At higher PMe_3 concentrations (0.26 M, Figure 3c), both coordinated ligands exchange rapidly so that only a broad resonance is observed for the free and the coordinated phosphine. The signals corresponding to the methylene group and the Pd-bound aromatic carbon of **2a** appear as doublets of doublets due to their coupling with the *trans* and *cis* phosphorus nuclei. On addition of PMe_3, the signal due to the methylene group collapses into a broad singlet (Figure 1c), while the quaternary aromatic resonance remains a broad doublet, with a typically high *trans*-J_{CP} constant of 123 Hz. This indicates that the ligand located in *trans* to the methylene group exchanges faster, doubtless due to the stronger *trans* effect of the latter, as compared to the aryl fragment. Values of $\Delta G^{\ddagger}$ (at 298 K) for the exchange of the PMe_3 ligands *cis* and *trans* to the CH_2 group of 13.3(8) and 12.1(4) kcal/mol, respectively, have been determined by line-shape simulation of the $^{31}P\{^1H\}$ spectrum of a 0.1 M solution of **2a** in CD_2Cl_2 containing added PMe_3 (0.15 M); spectra were recorded at ten different temperatures between 227 and 326 K (see Supporting Information).

The higher *trans* effect of the methylene group becomes also apparent in the selective substitution of the *trans* PMe_3 ligand by *tert*-butyl isocyanide, to give the mono(isocyanide) complex **2h** (Scheme 3). The thermodynamic preference for this substitution pattern is demonstrated by the formation of the same isomer in the reaction of the bis(isocyanide) derivative **2e** with PMe_3. The same trend was also observed in the analogous nickel system, where the PMe_3 ligand *trans* to the methylene group can be selectively displaced by pyridine[2a] or *t*-BuNC.[2c] As already noted, this substitution pattern governs the regioselectivity of the insertion reactions of these metallacycles.[2c,d]

Insertion Reactions. The insertion of small molecules into the M−C bonds of metallacycles often leads to the formation of carbo- or heterocyclic compounds that may be difficult to prepare by other methods. We have studied the reactivity of the palladacycles **2** toward several molecules amenable to participate in such insertion reactions and have found that these compounds are much less prone to undergo migratory insertion reactions than the related nickel compounds. Thus, in contrast with the ready carbonylation of $Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)(PMe_3)_2$, neither **2a** or **2b** react with CO under rather forcing conditions (80 °C, 20 atm). Similarly, no reaction was observed when these complexes were brought into contact with CO_2, CS_2, or other heterocumulenes known to insert readily into the Ni−C bonds of the analogous Ni metallacycles.[2d] In fact, the metallacycle **2b** constitutes a rare example of stable Pd−aryl-alkene complex. Few compounds of this kind are known, migratory insertion of

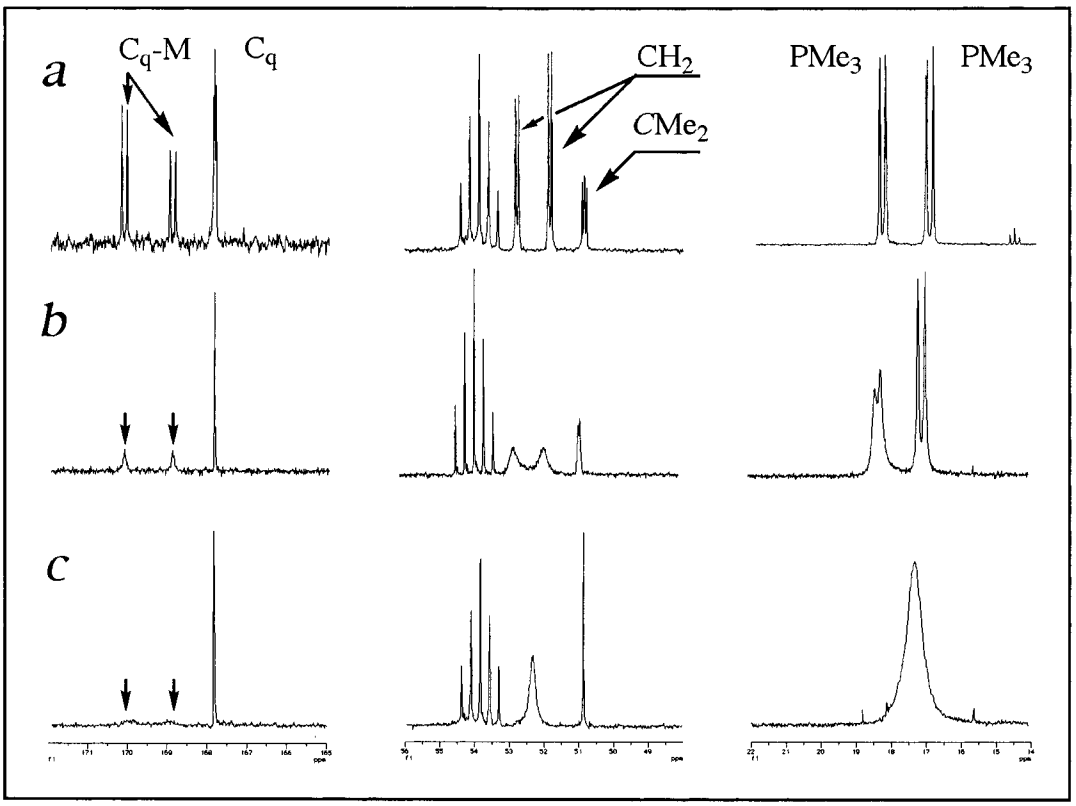
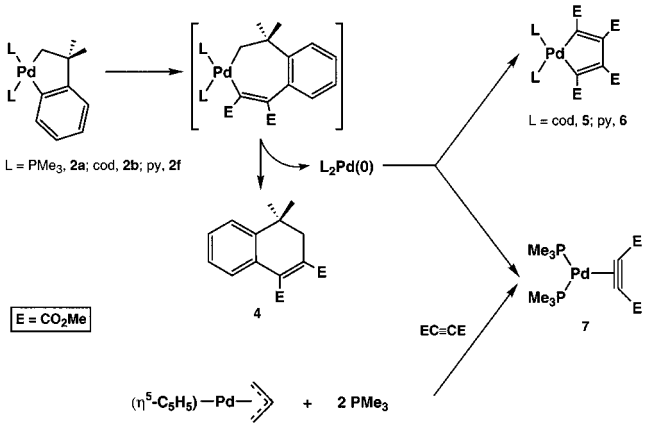


Figure 3. Selected zones of the 100 MHz $^{13}C\{^1H\}$ NMR spectrum of **2a**. (a) 0.24 M solution in CD_2Cl_2. (b) and (c) the same spectrum recorded in the presence of free PMe_3, 0.02 and 0.26 M, respectively.

the olefin into Pd−aryl bonds is a very favorable rearrangement, even for Pd−cyclooctadiene complexes with relatively inert perfluoroaryl groups.[11] The stability of **2b** is probably due to the difficulty experienced by the rigid metallacycle and the cyclooctadiene ligand to attain the geometry of the insertion transition state.

It has been reported that nickel and palladium metallacarbocycles insert acetylenes leading to different organic products.[2c,7,8b,c,12] Once more, in contrast with the high reactivity of the nickel analogue of **2a**, the palladacycles **2a**, **2b**, and **2f** react only with alkynes that bear electron-withdrawing substituents. Dimethyl acetylenedicarboxylate (dmad) gives rise to the 2,3-dihydronaphthalene derivative **4** (Scheme 4), which by analogy with the related Ni chemistry, can be assumed to form by insertion of the alkyne into the Pd−aryl bond, followed by reductive elimination.[2b] The final fate of the palladium atom depends on the co-ligand present in the metallacycle. Thus, the cod and pyridine complexes, **2b** and **2f**, give rise, respectively, to the known palladacyclopentadienes **5**[13b] and **6**.[13c] These products have been reported to form in the reaction of Pd(0) species with dmad.[13] In contrast, the PMe_3 derivative **2a** leads to the unstable Pd(0) alkyne complex **7**, which could not be isolated in a pure state, owing to its low melting point and its

Scheme 4



reduced thermal stability. However, its identity was authenticated by comparison of its spectroscopic data with those of a sample prepared independently from Pd(η^5-C_5H_5)(η^3-C_3H_5), PMe_3 and dmad.

Catellani[8a] has shown that palladium metallacycles that contain methyl isonicotinate as a coligand can react with alkynes less activated than dmad. In a similar fashion, the 4-cyanopyridine complex **2g** reacts with methyl propiolate to afford a 5:1 mixture of the dihydronaphthalene isomers **8** and **8′** (eq 1). Neither palladacyclopentadiene nor Pd(0)−alkyne complexes were detected in this reaction. The regioselectivity displayed is in line with that of the nickel analogue of **2a**, and also with Catellani's results, and favors the organic product in which the more electronegative substituent of the alkyne ends up in the position adjacent to the methylene group. This analogy gives some additional support to the mechanistic proposal of Scheme 4.

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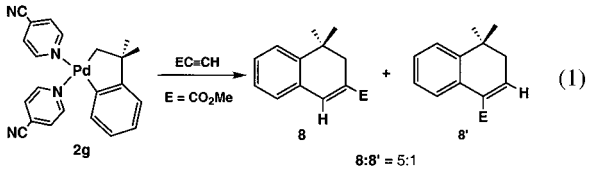


(1)

Many transition metal alkyls undergo facile insertion reactions with SO_2.[14] This reaction leads to sulfinate complexes and can be exploited for the preparation of sulfinic acids.[15a−c] Additionally, it has been suggested that Pd complexes may catalyze the formation of polysulfones by alternating insertion of ethylene and SO_2, much in the same way as the well-known copolymerization of CO and olefins.[14a, 15d,e]

On exposure to 1 equiv of SO_2 at 0 °C, solutions of **2a** inmediately develop an intense orange coloration which gradually fades into a pale yellow color. This reaction leads to the formation of two products, **10** and **11** (Scheme 5), with a remarkable solvent dependence, to the point that compound **11** is formed selectively in solvents such as CH_2Cl_2, MeCN, or Me_2CO, whereas the use or diethyl ether or toluene leads to mixtures of **10** an **11**. It is worth pointing out that whereas **11** is always the major product, the two compounds form in a poorly reproducible ratio, albeit in nearly quantitative combined yield. The analytical and spectroscopic data indicate that they are isomeric *S*-sulfinate complexes, arising from the insertion of one molecule of SO_2 into a Pd−C bond. Thus, they display two strong infrared absorptions in the 1000−1200 cm^{-1} range, characteristic of the sulfinate functionality (**10**, 1146, 1064 cm^{-1}; **11**, 1155, 1036 cm^{-1}). The $^{13}C\{^1H\}$ NMR spectra of **10** and **11** show that these compounds differ in the site of insertion of the molecule of SO_2. Thus, the typically large *trans*-$^{13}C-^{31}P$ coupling (>90 Hz) is missing in the methylene signal of **10**, as well as in the initially Pd-bound aromatic quaternary resonance of **11**, which leads to the conclusion that they result from the insertion of SO_2 into the Pd−CH_2 and the Pd−C(aryl) bonds of **2a**, respectively (see Scheme 5). The proposed structure of **10** has been confirmed by single-crystal, X-ray methods (Figure 4).

Even though attempts to grow suitable crystals of **11** did not meet with success, upon leaving a methanol solution of this complex to stand for 15 days at −20 °C in a septum-capped Schlenk tube, crystals of a fairly insoluble compound, **12**, were formed. Its X-ray structure (Figure 5) shows that **12** is a dimer, resulting from the loss of the PMe_3 ligand *trans* to the methylene group of **11**. Compound **12** is sparingly soluble in CD_2Cl_2, where its NMR spectra can be recorded. These are in full accord with its solid-state structure, and show the presence of a single PMe_3 ligand *cis* to the methylene group.

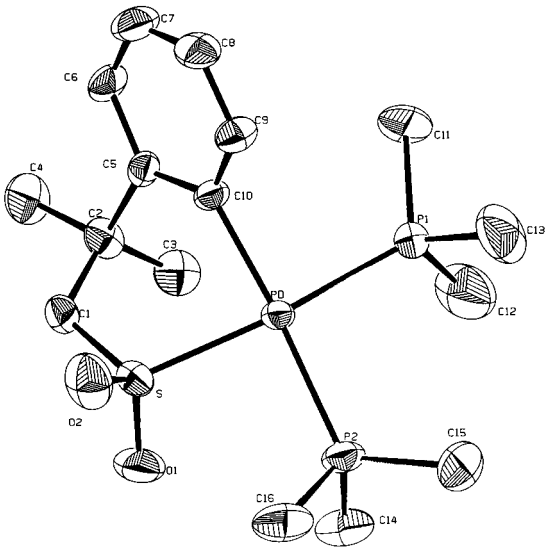
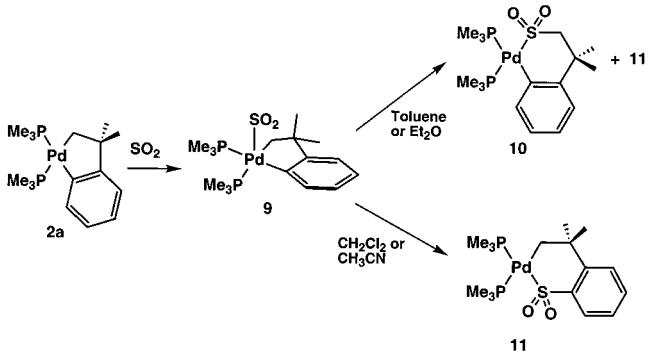
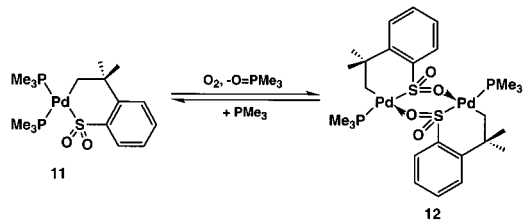


Figure 4. Crystal structure of complex **10**.

Scheme 5



Compound **11** is rapidly generated by addition of PMe_3 to a suspension of **12** in methanol. Obviously, the low solubility of the latter complex favors its formation, but this requires dissociation of PMe_3, which becomes subsequently oxidized by adventitious oxygen. Accordingly, large crystals of **12** can be readily obtained upon exposure of methanolic solutions of **11** to air for 1−2 days (eq 2).



(2)

Single and double insertions of SO_2 into the M−C bonds of group 10 dialkyl or metallacyclic complexes are known.[14] In our case, subjecting solutions of **10** and **11** to 3 atm of SO_2 (100 °C, 12 h) does not result in further insertion chemistry. Additionally, in the absence of SO_2, toluene solutions of **10** or **11** do not isomerize or extrude sulfur dioxide. Hence it can be assumed that under these conditions the formation of the two compounds is irreversible.

Although the analogies in the bonding of CO and SO_2 to metal in their complexes[16] suggest that the insertion of these molecules might follow similar pathways (i.e., migratory insertion), in most cases the insertion of SO_2 is thought to proceed by a direct electrophilic attack at the metal-bound

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(15) (a) Pelzer, G.; Keim, W. *J. Mol. Catal. A* **1999**, *139*, 235. (b) Herwig, J.; Keim, W. *Inorg. Chim. Acta* **1994**, *122*, 381. (c) Keim, W.; Herwig, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1592. (d) Jurgen, J. Thesis, Rheinish-Westfalischen Tecnische Hohschule Aachen, 1995. (e) Klein, H. S. *J. Chem. Soc., Chem. Commun.* **1968**, 377.

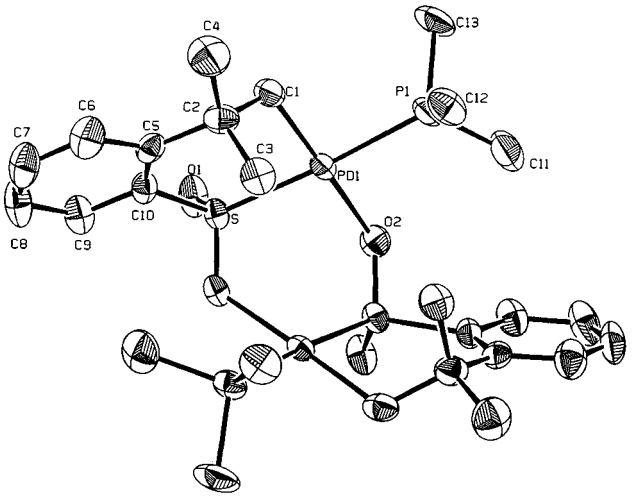
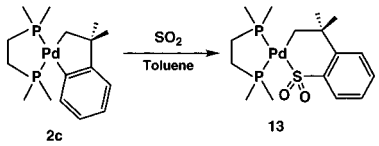


Figure 5. Crystal structure of compound **12**.

carbon atom. However, Brookhart has recently reported that the insertion of sulfur dioxide into the Pd−Me bond of the cationic complex $[PdMe(Et_2O)(dppe)]^+$ is preceded by the displacement of the coordinated molecule of Et_2O by SO_2,[14a] suggesting an intramolecular insertion mechanism. Apart from this example, we are not aware of other cases of intramolecular insertion of a coordinated molecule of SO_2. Interestingly, the observation of a transient orange coloration during the reaction of **2a** with SO_2 suggests the existence of a detectable intermediate,[17] and this prompted us to undertake a low-temperature NMR study. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of samples of **2a** dissolved in CD_2Cl_2, acetone-d_6, and toluene-d_8 were recorded at −80 °C before and after treatment with ca. 1.7 equiv of SO_2. In all the experiments, the NMR spectra showed the conversion of **2a** into a single new species, **9**. Although the spectra of **9** and **2a** are similar, their signals are significantly displaced (see Experimental Section). For example, in CD_2Cl_2 and acetone-d_6, the resonances due to the methylene group of **9** are shifted to low field by ca. 0.64 ppm in the ^1H and 10 ppm in the $^{13}C\{^1H\}$ NMR spectra. The shifts are less pronounced in toluene-d_8 (0.3 and 6.7 ppm, respectively), but the variation upon conversion of **2a** into **9** is also evident in this solvent. The fact that **9** is a SO_2 complex[18] and not an insertion product is revealed by the ^{13}C resonances due to the palladium bound carbon atoms, which appear splitted into doublets of doublets by coupling with the phosphorus nuclei, displaying characteristic *trans*-$^2J_{CP}$ values higher than 80 Hz. These coupling constants are indicative of a square pyramidal geometry in which both the Pd-bound carbon atoms and the phosphine ligands preserve their relative positions as in **2a**. The methyl substituents of the metallacyclic fragment give rise to a broad resonance in the ^{13}C spectra, possibly due to intermolecular exchange of the coordinated SO_2.

As the temperature of the samples of **9** rises, insertion of SO_2 to give the final products proceeds without any other intermediate being observed. As previously discussed, the SO_2 insertion leads selectively to **11** in CD_2Cl_2 and acetone-d_6 and to a mixture of **10** and **11** in toluene-d_8. The reaction is noticeable above −60 °C in the former solvents, and slower in toluene, where the insertion takes place at around −20 °C. No significant changes can be detected in the shape or the chemical shifts of the ^1H and $^{31}P\{^1H\}$ signals of **9** up to 0 °C (Figure 6). This suggests that SO_2 insertion takes place directly from the pentacoordinated species **9**. In agreement with this observation, the metallacycle **2c**, bearing the chelating diphosphine dmpe as a coligand, also reacts readily with SO_2, affording selectively complex **13** (eq 3), i.e., the product of insertion into the Pd−aryl bond.



2c 13 (3)

Crystal Structures of 2a, 2b, 10, and 12. Figures 1 and 2 show the crystal structures of the metallacycles **2a** and **2b**, which differ only in the nature of the ancillary ligand. In both complexes, the central Pd atom is in a square planar environment distorted by the chelating organic ligand that imposes acute CH_2−Pd−aryl bond angles of 77.4(5)° and 79.08°(13), respectively. Both rings are appreciably puckered (puckering angle: 47.90(2)°, **2a**; 37.0(2)°, **2b**), with the methylenic carbon placed well above the mean plane formed by the remaining atoms in the metallacycle. In **2a**, the steric repulsion between the aryl ring and the adjacent PMe_3 ligand induces a slight tetrahedral distortion which was also observed in the Ni analogue.[2a] This distortion is not apparent in **2b**, where such steric interactions are absent. Thus, the planes defined by the Pd, C1 and C6 and Pd, P1 and P2 in **2a** form an angle of 10.21(2)°, while the analogous measurement for **2b**, considering the geometric centers of the olefinic bonds as the attachment points of the cod ligand, amounts only to 1.3(4)°. Although the reactivity and thermal stability of **2a** does not differ significantly from that of **2b**, it has been shown that related palladium metallacycles can be destabilized by the introduction of substituents in the aromatic ring position next to the metal center.[8a]

The two Pd−P bond lengths in **2a** are 2.310(4) and 2.341(3) Å, with the longer distance corresponding to the phosphorus atom *trans* to the methylene group. A similar trend was also found in **2b**, where the distance from the Pd atom to the geometric centers of the cyclooctadiene double bonds are 2.231-(4) (*trans* to CH_2) and 2.193(4) Å (*trans* to the aromatic ring). The dissimilarity of the metal−ligand distances is a clear reflection of the larger *trans* influence of the alkyl functionality.

Figures 4 and 5 contain ORTEP views for compounds **10** and **12**, respectively. Both molecules display the *S*-sulfinate functionality that arises from SO_2 insertion[19] but differ in the site of the insertion. Compound **12** consists of two identical metallacyclic fragments. The coordination of an oxygen atom from each sulfinyl group to the palladium center of the neighboring fragment gives rise to a boat-shaped six-membered ring. This configuration brings the coordination planes of the palladium atoms face to face, but the Pd−Pd distance (3.586 Å) is too long to allow any bonding interaction.

The preferred conformation of the metallacyclic rings of **10** and **12** depends markedly on the position of the SO_2 unit. Thus,

(16) (a) Mingos, D. M. P. *Trans. Met. Chem.* **1978**, *3*, 1. (b) Kubas, G. J. *Acc. Chem. Res.* **1994**, *27*, 183. (c) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 18. (d) Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 32.

(17) Somewhat similar color changes have been noted in an analogous reaction involving SO_2 and Pt compounds. See: ref 17a and 17b.

(18) (a) Albrecht, M.; Gossage, R. A.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1998**, 1003. (b) Albrecht, M.; Lutz, M.; Spek, A. L.; van Koten, G. *Nature* **2000**, *406*, 970. (c) Livingstone, S. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. G., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, p 634. (d) Hill, A. F. *Adv. Organomet. Chem.* **1994**, *36*, 159.

(19) For further examples of X-ray characterized palladium *S*-sulfinates, see: Tuntulani, T.; Musie, G.; Reibenspies J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1995**, *34*, 6279.

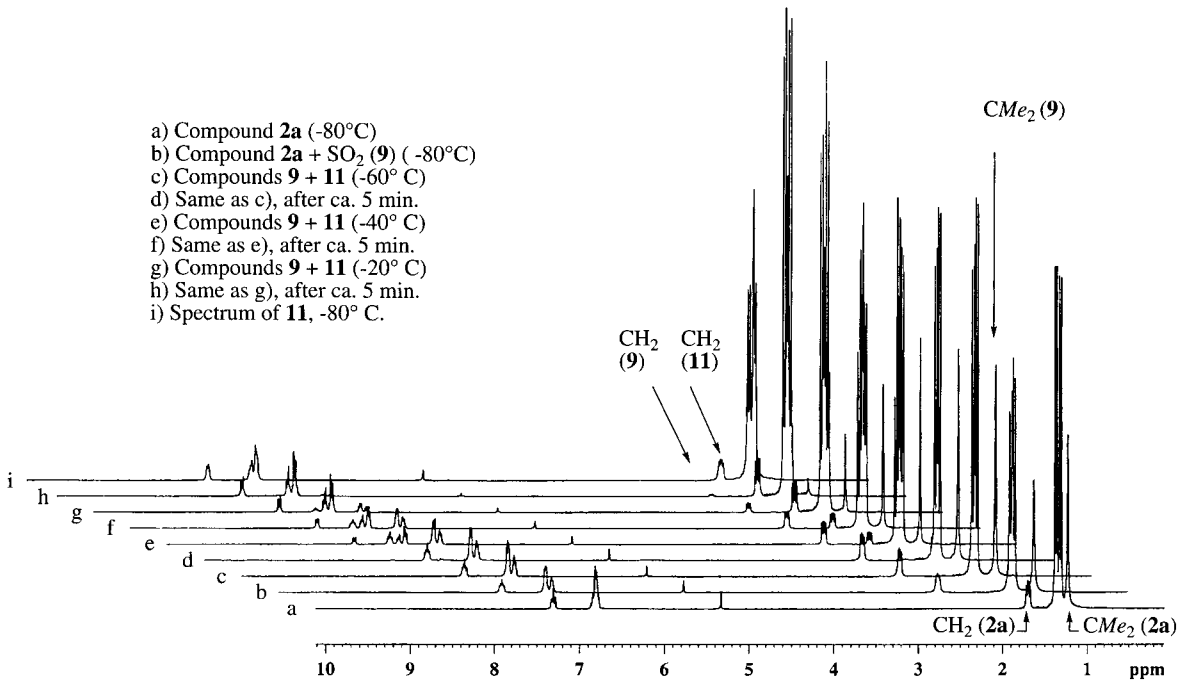


Figure 6. ^{1}H NMR monitoring of the transformation **2a** → **9** → **11** in CD_2Cl_2.

complex **10** adopts a boat conformation while each metallacyclic half of **12** is found as a half-chair, with the methylene group markedly departing from the nearly planar unit formed by the Pd, S, C2, C5, and C10 atoms.

The larger size of the metallacycle rings in **10** and **12**, as compared to **2a** and **2b**, allow S−Pd−C bond angles close to the ideal 90° values (85.9(2)° and 87.6(2)° respectively). However, and similarly to **2a**, the phosphine and the aryl ligands of **10** also cause a slight tetrahedral distortion of the palladium environment of this compound.

Conclusions

The cyclometalation of Ni, Pd, and Pt neophyl complexes provides access to a family of metallacyclic derivatives that illustrate important differences in the chemistry of these metals. The striking difference in the conditions required for the synthesis of the palladium derivatives with respect to those previously found for the Ni and Pt analogues suggests the formation of these metallacycles may involve different C−H activation mechanisms. The comparison of the structural and chemical properties of the Ni and Pd metallacycles evidences a number of closely related features, in particular with regards to the ligand substitution pattern, controlled by the different labilizing effects exerted by the methylene and the aryl groups. Although these effects seem to influence the regioselectivity of the insertion reactions in the same direction for both metals (Ni and Pd), the cyclometalated Pd-neophyl complexes show much lower tendency to undergo migratory insertion reactions than the Ni analogues. Pd metallacycles have nevertheless found to display an interesting reactivity toward strong electrophilic reagents such as SO_2, whose intimate aspects are far from being understood. Further studies on the mechanism of the cyclometalation of the neophyl complexes of group 8 and the reactivity of the resulting metallacycles are currently under way in our laboratories.

Experimental Section

Microanalyses were performed by the Analytical Service of the University of Seville and the Instituto de Investigaciones Químicas. The spectroscopic instruments used were Perkin-Elmer Models 684 and 883 and Bruker Model Vector 22 for IR spectra, and Bruker AMX-300, DRX-400, AMX-500, and DRX-500 for NMR spectroscopy. The ^{13}C resonance of the solvent was used as an internal standard, but chemical shifts are reported with respect to $SiMe_4$. The $^{13}C\{^1H\}$ NMR assignments were helped in most cases with the use of gate-decoupling techniques. $^{31}P\{^1H\}$ NMR shifts are referenced to external 85% H_3PO_4. Gas chromatography was performed in a Thermoquest trace GC Cromatograph, equipped with an Automass Multi Mass Spectrometer. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40−60 °C. The compounds $PdCl_2(cod)_2$ (cod = 1,5-cyclooctadiene),[20] $Pd(CH_2CMe_2C_6H_5)Cl(cod)$,[6c] $Pd(CH_2CMe_2C_6H_5)Cl(PMe_3)_2$,[6c] $[PdCl(\eta^3\text{-}C_3H_5)]_2$,[21] phosphine PMe_3,[22] and the isonitrile, Bu^tNC,[23] were prepared according to literature methods. $Na(2,5\text{-}Me_2C_4H_2N)$ and NaCp were obtained by reacting NaH with $2,5\text{-}Me_2C_4H_2NH$ and freshly cracked dicyclopentadiene, respectively.

Thermolysis of $Pd(CH_2CMe_2Ph)_2(PMe_3)_2$. A solution containing 0.4 g (0.08 mmol) of the title compound in 10 mL of Et_2O was heated at 55 °C for 3h. The resulting black suspension was evaporated under vacuum, the residue extracted with 2 × 0.5 mL of C_6D_6, and the solution filtered through a small pad of silica. The ^{1}H NMR spectrum of this solution showed the presence of a pure compound identified as 2,4-dimethyl-2,4-diphenylhexane (bineophyl) by comparison with published NMR data.[24] This compound was isolated in nearly quantitative yield by evaporation of the solvent.

The same reaction was also carried out in an NMR tube, using C_6D_6 as a solvent, and monitored by ^{1}H NMR and $^{31}P\{^1H\}$ NMR. Bineophyl was formed cleanly, along with free PMe_3 and a black precipitate of palladium. CI MS: 266 (M^+). ^{1}H NMR (C_6D_6, 20 °C) δ 1.12 (s, 12H, CMe_2), 1.14 (s, 4H, CH_2), 7.07 (m, 1 H, CH_{ar}), 7.15 (m, 4H, CH_{ar}); $^{13}C\{^1H\}$ (C_6D_6, 20 °C) δ 29.2 (s, CMe_2), 37.5 (s, CMe_2), 39.2 (s, CH_2), 125.7, 126.2, 128.3 ($C_{ar}H$), 149.3 (C_{ar}).

(20) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 47.
(21) Tatsuno, Y.; Yoshida, T.; Otsika, S. *Inorg. Synth.* **1990**, *28*, 343.
(22) Luetkens, M. L., Jr., Sattelberger, A. P.; Murray, H. H.; Basil, J. D.; Fackler, J. P., Jr. *Inorg. Synth.* **1990**, *28*, 305.
(23) Gokel, G. W.; Widera, R. P.; Weber, W. P. *Org. Synth.* **1976**, *55*, 96.
(24) Whitesides, G. M.; Panek, E. J.; Steronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 232.

Synthesis of Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(PMe$_3$)$_2$, 2a. Method A. To a cooled (−30 °C) suspension of **2b** (0.34 g, 1 mmol) in 30 mL of Et$_2$O was added 2 mL of a 1 M solution of PMe$_3$ (2 mmol) in THF. After removing the cold bath, the mixture was stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure and the oily residue extracted with 15 mL of Et$_2$O. Filtration, partial concentration of the solvent and addition of some petroleum ether, provided, upon cooling to −30 °C white crystals of **2a** in quantitative yield.

Method B. A solution of the complex Pd(CH$_2$CMe$_2$C$_6$H$_5$)Cl(PMe$_3$)$_2$, **1a** (0.21 g, 0.5 mmol) in 30 mL of Et$_2$O was cooled at −50 °C and treated with NaN(SiMe$_3$)$_2$ (0.5 mmol, 0.85 mL of a 0.6 M solution in toluene). The mixture was allowed to reach room temperature and then stirred at 50 °C for 5 h, during which time the color of the solution turned dark gray. The reaction mixture was taken to dryness and the residue extracted with 30 mL of Et$_2$O. Afterwards, filtration and concentration of the solution to ca. 5−10 mL, addition of some petroleum ether, and cooling to −30 °C, gave white crystals of **2a** in 65% yield.

The use of NaOH or NaBu^{t}O, as the base provides complex **2a** in 60% or 45% yield, respectively.

Anal. Calcd for C$_{16}$H$_{30}$P$_2$Pd: C, 49.2; H, 7.7. Found: C, 49.2; H, 7.6. ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 0.85 (d, 9 H, $^2J_{HP}$ = 6.7 Hz, PMe$_3$), 0.90 (d, 9 H, $^2J_{HP}$ = 6.7 Hz, PMe$_3$), 1.77 (s, 6 H, CMe$_2$), 2.20 (dd, 2 H, $^3J_{HP}$ = 5.7 and 8.8 Hz, CH$_2$), 7.27 (m, 3 H, CH$_{ar}$), 7.63 (tm, 1 H, CH$_{ar}$); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C) AX spin system, δ_A = −27.9, δ_X = −22.9, J_{AX} = 23 Hz; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C) δ 16.3 (d, $^1J_{CP}$ = 19 Hz, PMe$_3$), 17.7 (dd, $^2J_{CP}$ = 3, $^1J_{CP}$ = 17 Hz, PMe$_3$), 35.5 (d, $^4J_{CP}$ = 9 Hz, C*Me*$_2$), 50.9 (t, $^3J_{CP}$ = 6 Hz, *C*Me$_2$), 52.5 (dd, $^2J_{CP}$ = 9 and 95 Hz, CH$_2$), 122.1 (d, J_{CP} = 3 Hz, C$_{ar}$H), 123.2 (s, C$_{ar}$H), 123.7 (d, J_{CP} = 10 Hz, C$_{ar}$H), 138.0 (dd, J_{CP} = 5 and 11 Hz, C$_{ar}$H), 167.0 (s, C$_{ar}$), 169.2 (dd, $^2J_{CP}$ = 14 and 123 Hz, C$_{ar}$).

In an additional, NMR-monitored study, 0.011 g (0.023 mmol) of compound **3** (vide infra) was dissolved in 0.6 mL of CD$_2$Cl$_2$ and placed in an NMR tube. The NMR probe was heated at 50 °C and spectra were adquired every 30 min during 10 h. After this time, an equilibrium mixture of compounds **3**, **2a**, and pyrrole was attained.

Synthesis of Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(cod), 2b. Method A. To a solution of Pd(CH$_2$CMe$_2$C$_6$H$_5$)Cl(cod), **1b** (0.38 g, 1 mmol) in THF (30 mL), NaOH (0.12 g, 3 mmol), and H$_2$O (0.3 mL) were added. The mixture was stirred at room temperature for 2−3 h and then taken to dryness. The residue was extracted with Et$_2$O and filtered. The filtrate was concentrated and some petroleum ether added. Cooling to −30 °C furnished complex **2a** as white crystals in 65% yield.

Method B. 10 mL of a 1 M solution of Mg(CH$_2$CMe$_2$C$_6$H$_5$)Cl (10 mmol) in Et$_2$O was added to a cooled (−70 °C) solution of PdCl$_2$(cod) (2.85 g, 10 mmol) in 120 mL of Et$_2$O. The mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum and the residue extracted with 150 mL of CH$_2$Cl$_2$ and centrifuged. The solution of the alkyl Pd(CH$_2$CMe$_2$C$_6$H$_5$)Cl(cod) formed was treated with an excess of NaOH (1.2 g, 30 mmol) and 0.5 mL of water, and the resulting suspension stirred at room temperature for 2 h and filtered through silica. The filtrate was partially evaporated under reduced pressure and some petroleum ether added. After cooling to −30 °C, compound **2a** was obtained as white crystals in 70% yield.

Anal. Calcd for C$_{18}$H$_{24}$Pd: C, 62.3; H, 6.9. Found: C, 62.4; H, 7.0. ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 1.80−2.00 (m, 8 H, CH$_2$ cod), 1.57 (s, 6 H, CMe$_2$), 2.54 (s, 2 H, CH$_2$), 5.16 (s, 2 H, CH cod), 5.67 (s, 2 H, CH cod), 7.15 (tm, 2 H, CH$_{ar}$), 7.22 (tm, 1 H, CH$_{ar}$), 7.27 (dm, 1 H, CH$_{ar}$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C) δ 28.2, 28.9 (s, CH$_2$ cod), 34.0 (s, C*Me*$_2$), 49.7 (s, *C*Me$_2$), 53.4 (s, CH$_2$), 109.9, 113.2 (s, CH cod), 123.1, 124.5, 124.8, 134.6 (s, C$_{ar}$H), 162.5, 167.5 (s, C$_{ar}$).

Synthesis of Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(dmpe), 2c. To a cooled (−30 °C) suspension of complex **2b** (0.34 g, 1 mmol) in 30 mL of Et$_2$O, was added dmpe (1 mmol, 1 mL of a 1 M solution in THF). The cooling bath was removed and the mixture stirred at room temperature for 1 h, and then taken to dryness. The residue was extracted with a mixture of CH$_2$Cl$_2$−petroleum ether and the solution cooled to −30 °C. Compound **2c** was obtained as white crystals in quantitative yield. Anal. Calcd for C$_{16}$H$_{28}$P$_2$Pd: C, 49.4; H, 7.2. Found: C, 49.2; H, 7.2. ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 0.80−0.90 (m, 4 H, P−CH$_2$), 0.88 (d, 6 H, $^2J_{HP}$ = 6.9 Hz, PMe$_2$), 0.95 (d, 6 H, $^2J_{HP}$ = 6.9 Hz, PMe$_2$), 1.77 (s, 6 H, CMe$_2$), 2.43 (t, 2 H, $^3J_{HP}$ = 7.0 Hz, CH$_2$), 7.35 (m, 3 H, CH$_{ar}$), 7.78 (tm, 1 H, CH$_{ar}$); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C) AX spin system, δ_A = 11.7, δ_X = 18.4, J_{AX} = 7 Hz; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C) δ 12.5 (d, $^1J_{CP}$ = 14 Hz, PMe$_2$), 13.0 (d, $^1J_{CP}$ = 18 Hz, PMe$_2$), 27.0−29.0 (m, P−CH$_2$), 36.0 (d, $^4J_{CP}$ = 6 Hz, C*Me*$_2$), 46.1 (dd, $^2J_{CP}$ = 7 and 96 Hz, CH$_2$), 50.8 (t, $^3J_{CP}$ = 6 Hz, *C*Me$_2$), 122.8 (d, J_{CP} = 3 Hz, C$_{ar}$H), 123.4 (s, C$_{ar}$H), 124.0 (d, J_{CP} = 10 Hz, C$_{ar}$H), 139.8 (dd, J_{CP} = 5 and 13 Hz, C$_{ar}$H), 168.5 (sa, C$_{ar}$), 169.2 (dd, $^2J_{CP}$ = 10 and 125 Hz, C$_{ar}$).

Synthesis of Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(bipy), 2d. To a suspension of compound **2b** (0.34 g, 1 mmol) in Et$_2$O (20 mL) cooled at −50 °C was added a solution of bipy (0.16 g, 1 mmol) in Et$_2$O (10 mL). The cooling bath was removed with continued stirring; when the mixture developed a yellow coloration, some microcrystalline solid precipitated. After further stirring for 1 h at room temperature the suspension was filtered and the solid washed with petroleum ether and dried. Recrystallization from CH$_2$Cl$_2$−petroleum ether gave yellow crystals in 90% yield. Anal. Calcd for C$_{20}$H$_{20}$N$_2$Pd: C, 60.8; H, 5.1; N, 7.1. Found: C, 61.1; H, 5.2; N, 7.1. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C) δ 1.39 (s, 6 H, CMe$_2$), 2.37 (s, 2 H, CH$_2$), 6.80 (m, 1 H, CH$_{ar}$), 6.93 (m, 2 H, CH$_{ar}$), 7.49 (m, 1 H, CH$_{ar}$), 7.58 (m, 2 H, CH$_{ar}$), 8.00 (m, 2 H, CH$_{ar}$), 8.12 (m, 2 H, CH$_{ar}$), 8.75 (d, 1 H, J_{HH} = 4.4 Hz, CH$_{ar}$), 9.17 (d, 1 H, J_{HH} = 4.4 Hz, CH$_{ar}$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C) δ 35.7 (s, C*Me*$_2$), 47.1 (s, CH$_2$), 49.4 (s, *C*Me$_2$), 123.7, 124.0, 124.9, 126.0, 127.6, 127.8, 136.8, 139.8, 151.2, 152.1 (s, CH$_{ar}$), 156.4, 156.7, 162.1, 171.1 (s, C$_{ar}$).

Synthesis of Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(Bu^{t}NC)$_2$, 2e. A total of 2 mL of a 1 M solution of Bu^{t}NC (2 mmol) in Et$_2$O was added to a suspension of complex **2b** (0.34 g, 1 mmol) in 30 mL of Et$_2$O cooled at −30 °C. The mixture was stirred at room temperature for 1 h. The solvent was stripped off and the residue extracted with Et$_2$O, and filtered. After partial evaporation of the solvent, cooling to −30 °C provided compound **2e** as white crystals in 90% yield. Anal. Calcd for C$_{20}$H$_{30}$N$_2$Pd: C, 59.3; H, 7.4; N, 6.9. Found: C, 59.4; H, 7.1; N, 6.8. IR (Nujol mull): 2188, 2166 cm^{-1} (υ(CN)). ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 0.83 (s, 9 H, Bu^t), 0.90 (s, 9 H, Bu^t), 1.73 (s, 6 H, CMe$_2$), 2.65 (s, 2 H, CH$_2$), 7.23 (m, 3 H, CH$_{ar}$), 7.97 (m, 1 H, CH$_{ar}$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C) δ 29.4, 29.5 (s, *Me*$_3$C), 35.3 (s, C*Me*$_2$), 44.3 (s, CH$_2$), 50.7 (s, *C*Me$_2$), 55.9 (s, Me$_3$*C*), 122.7, 123.7, 124.0, 139.6 (s, C$_{ar}$H), 144.3 (ta, Bu^{t}N*C*), 145.2 (t, $^1J_{CN}$ = 7 Hz, Bu^{t}N*C*), 164.7, 167.7 (s, C$_{ar}$).

Synthesis of Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(py)$_2$, 2f. To a suspension of compound **2b** (0.34 g, 1 mmol) in Et$_2$O (30 mL) cooled to −30 °C, 0.16 mL (2 mmol) of pyridine was added. The mixture was stirred at room temperature for 1 h and a white solid precipitated. The solvent was removed under vacuum and the solid washed with petroleum ether and dried. It was recrystallized from CH$_2$Cl$_2$ and obtained as white crystals in 90% yield. Anal. Calcd for C$_{20}$H$_{22}$N$_2$Pd: C, 60.5; H, 5.5; N, 7.0. Found: C, 60.4; H, 5.6; N, 7.0. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C) δ 1.33 (sa, 6 H, CMe$_2$), 2.02 (sa, 2 H, CH$_2$), 6.42 (da, 1 H, J_{HH} = 6.3 Hz, CH$_{ar}$), 6.60 (ta, 1 H, J_{HH} = 7.0 Hz, CH$_{ar}$), 6.73 (da, 1 H, J_{HH} = 7.3 Hz, CH$_{ar}$), 6.81 (ta, 1 H, J_{HH} = 7.3 Hz, CH$_{ar}$), 7.28 (sa, 2 H, py), 7.36 (sa, 2 H, py), 7.73 (sa, 1 H, py), 7.79 (sa, 1 H, py), 8.47 (sa, 2 H, py), 8.79 (sa, 2 H, py); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C) δ 35.8 (s, C*Me*$_2$), 44.0 (s, CH$_2$), 49.5 (s, *C*Me$_2$), 123.6, 124.3, 125.4 (s, C$_{ar}$H), 126.7 (s, 4 C$_{ar}$H py), 137.4 (s, C$_{ar}$H), 138.8 (s, 2 C$_{ar}$H py), 152.8 (s, 2 C$_{ar}$H py), 153.2 (s, 2 C$_{ar}$H py), 161.0, 170.8 (s, C$_{ar}$).

Synthesis of Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(4-CNpy)$_2$, 2g. A cooled (−30 °C) suspension of complex **2b** (0.17 g, 0.5 mmol) in Et$_2$O (30 mL) was treated with a solution of 4-CNpy (0.1 g, 1 mmol) in 10 mL of Et$_2$O. When the mixture was warming to room-temperature some yellow solid precipitated, the stirring was continued for 1 h. The suspension was taken to dryness and the solid washed with petroleum ether. It can be crystallized from CH$_2$Cl$_2$ and isolated as yellow crystals in quantitative yield. Anal. Calcd for C$_{22}$H$_{20}$N$_4$Pd: C, 59.1; H, 4.5; N, 12.5. Found: C, 59.2; H, 4.7; N, 12.8. IR (Nujol mull): 2232 cm^{-1} (υ(CN)). ^{1}H NMR (DMSO-d_6, 20 °C) δ 1.25 (s, 6 H, CMe$_2$), 1.96 (sa, 2 H, CH$_2$), 6.40 (sa, 1 H, CH$_{ar}$), 6.57 (t, 1 H, J_{HH} = 3.2 Hz, CH$_{ar}$), 6.65 (d, 1 H, J_{HH} = 6.4 Hz, CH$_{ar}$), 6.77 (ta, 1 H, J_{HH} = 6.1 Hz, CH$_{ar}$),

7.93 (d, 4 H, J_{HH} = 5.9 Hz, 4-CNpy), 8.91 (d, 4 H, J_{HH} = 5.1 Hz, 4-CNPy); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 20 °C) δ 33.8 (s, CMe_2), 43.2 (s, CH_2), 47.9 (s, *C*Me_2), 116.4, 119.9 (s, C_{ar}, 4CNpy), 121.4, 123.0, 123.5 (s, C_{ar}H), 126.3 (s, 4 C_{ar}H, 4-CNpy), 134.3 (s, C_{ar}H), 151.5 (s, 4 C_{ar}H, 4-CNpy), 160.5, 166.8 (s, C_{ar}).

Synthesis of Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(Bu^{t}NC)(PMe$_3$), 2h. Bu^{t}NC (1 mmol, 1 mL of a 1 M solution in Et_2O) was added to a solution of compound **2a** (0.39 g, 1 mmol) in Et_2O (30 mL) cooled at −30 °C. The mixture was stirred at room temperature for 1 h, the solvent evaporated under reduced pressure, and the residue extracted with Et_2O. After partial concentration of the solution, cooling to −30 °C furnished white crystals of compound **2h** in quantitative yield.

This complex can be similarly prepared in similar yield by treating complex **2e** with the stoichiometric amount of PMe_3. Anal. Calcd for $C_{18}H_{30}NPPd$: C, 54.3; H, 7.5; N, 3.5. Found: C, 54.7; H, 7.7; N, 3.5. IR (Nujol mull): 2160 cm^{-1} (υ(CN)). ^1H NMR (C_6D_6, 20 °C) δ 0.86 (s, 9 H, Bu^t), 0.96 (d, 9 H, $^2J_{HP}$ = 7.2 Hz, PMe_3), 1.76 (s, 6 H, CMe_2), 2.21 (d, 2 H, $^3J_{HP}$ = 8.7 Hz, CH_2), 7.37 (m, 3 H, CH_{ar}), 8.10 (m, 1 H, CH_{ar}); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C) δ −22.5 (s, PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 15.5 (d, $^1J_{CP}$ = 20 Hz, PMe_3), 29.6 (s, *Me*$_3$C), 35.5 (s, C*Me*$_2$), 46.7 (d, $^2J_{CP}$ = 9 Hz, CH_2), 50.9 (d, $^3J_{CP}$ = 8 Hz, *C*Me$_2$), 55.7 (s, Me$_3$*C*), 122.6 (d, J_{CP} = 3 Hz, C_{ar}H), 123.5 (s, C_{ar}H), 124.1 (d, J_{CP} = 9 Hz, C_{ar}H), 139.2 (s, C_{ar}H), 146.4 (sa, Bu^{t}N*C*), 167.5 (s, C_{ar}), 167.9 (d, $^2J_{CP}$ = 124 Hz, C_{ar}).

Synthesis of Pd(CH$_2$CMe$_2$C$_6$H$_5$)(2,5-Me$_2$C$_4$H$_2$N)(PMe$_3$)$_2$, 3. To a cooled (−70 °C) solution of Pd(CH$_2$CMe$_3$C$_6$H$_5$)Cl(PMe$_3$)$_2$ (0.42 g, 1 mmol) in 40 mL of THF, 0.37 mL (1 mmol) of a 2.7 M solution of Na(2,5-Me$_2$C$_4$H$_2$N) in THF was added. The cooling bath was removed and the mixture stirred at room temperature for 3 h. The solvent was removed under vacuum and the residue extracted with Et_2O (30 mL). After centrifugation, partial concentration of the solvent and cooling to −30 °C, compound **3** was isolated as orange crystals in 65% yield. Anal. Calcd for $C_{22}H_{39}NP_2Pd$: C, 54.4; H, 8.1; N, 2.9. Found: C, 54.5; H, 8.1; N, 2.9. ^1H NMR (CD_2Cl_2, 20 °C) δ 0.73 (t, 18 H, $J_{(app)HP}$ = 3.2 Hz, PMe_3), 1.50 (s, 6 H, CMe_2), 1.67 (t, 2 H, $^3J_{HP}$ = 9.2 Hz, CH_2), 2.57 (s, 6 H, *Me*$_2$C$_4$H$_2$N), 6.50 (s, 2 H, Me$_2$C$_4$*H*$_2$N), 7.0−8.0 (m, 5 H, CH_{ar}); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −16.2 (s, PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 15.0 (t, $J_{(app)CP}$ = 14 Hz, PMe_3), 17.8 (s, C*Me*$_2$), 25.2 (s, CH_2), 34.2 (s, *Me*$_2$C$_4$H$_2$N), 41.8 (s, *C*Me$_2$), 105.4 (s, CH_{ar} pirr), 120.0, 126.7, 127.0 (s, C_{ar}H), 132.2 (s, C_{ar} pirr), 155.5 (s, C_{ar}).

Reaction of Metallacycles 2b and 2f with MeO$_2$C≡CO$_2$Me (dmad). Synthesis of 4, 5 and 6. To a solution of complex **2b** (0.4 g, 1.16 mmol) in 30 mL of CH_2Cl_2 was added 0.34 mL (3.48 mmol) of dmad. Upon stirring for 3.5 h at room temperature the reaction mixture developed a dark red color. The solvent was stripped off and the residue extracted with petroleum ether and filtered. The remaining solid was identified as the crude palladacycle **5**. The filtrate was passed through a short silica column and concentrated to ca. 1 mL. The dihydronaphthalene **4** was isolated by spinning band chromatography, using a petroleum ether/Et_2O mixture (9:1) as eluant. Yield: 88%. The known palladacycle **5** was purified by recrystallization from a mixture CH_2Cl_2/petroleum ether (3:1) and obtained as yellow crystals in 83% yield.

The reaction of complex **2f** with dmad follows a similar course and gives the dihydronaphthalene **4** and complex **6**, isolated in 60% and 72% yield, respectively.

Reaction of Metallacycle 2a with MeO$_2$C≡CO$_2$Me (dmad). Synthesis of 4 and 7. Method A. A total of 0.37 mL (3 mmol) of dmad was added to a cooled (0 °C) solution of complex **2a** (0.39 g, 1 mmol) in 30 mL of Et_2O. The mixture was stirred at this temperature for 1 h, and then taken to dryness. The dark red oily residue was dissolved in Et_2O and the solution passed through a silica column, providing the organic compound **4** in 93% yield. The presence of complex **7** was ascertained by NMR spectroscopy ($^{31}P\{^1H\}$ and ^1H) of the crude reaction mixture, by comparison with spectra of an authentic sample prepared by Method B.

Method B. To a solution of 0.35 g (0.9 mmol) of [(η^3-C$_3$H$_5$)PdCl]$_2$ in THF (25 mL) cooled at −20 °C, CpNa (1.8 mmol, 4.6 mL of a 0.39 M solution in THF) was added. The mixture was stirred at this temperature for 1 h, at 20 °C for 30 min and then cooled again to −10 °C and treated with 0.22 mL (1.8 mmol) of dmad and 3.6 mL (3.6 mmol) of a 1 M solution of PMe_3 in THF. The resulting mixture was stirred at this temperature for 1 h and then taken to dryness. The red oily residue was identified as complex **7** by NMR.

^1H NMR (C_6D_6, 20 °C) δ 1.06 (d, 18 H, $^2J_{HP}$ = 7.2 Hz, PMe_3), 3.51 (s, 6 H, CO_2Me); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C) δ −21.4 (s, PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 18.5 (d, $^1J_{CP}$ = 22 Hz, PMe_3), 51.0 (s, CO_2*Me*), 137.0 (t, $^2J_{CP}$ = 45 Hz, −C≡C-), 165.3 (t, $^3J_{CP}$ = 16 Hz, *C*O$_2$Me).

Reaction of Metallacycle 2g with HC≡CO$_2$Me (dmad). Synthesis of 8 and 8′. To a solution of complex **2g** (0.33 g, 0.75 mmol) in 40 mL of CH_2Cl_2, methyl propiolate (209 μL, 2.25 mmol) was added, the color of the mixture changed from yellow to dark red. It was stirred 3.5 h at room temperature and then the solvent evaporated under reduced pressure. The dark red oily residue was extracted with petroleum ether and filtered. From the filtrate, compounds **8** and **8′** were isolated by spinning band chromatography, using petroleum ether, with 2% Et_2O, as eluant.

Isomer **8**: Spectroscopy data for this isomer has been reported previously[2c]. EI-HRMS: *m*/*z* 216.1142, M$^+$ (exact mass calculated for $C_{14}H_{16}O_2$ 216.1150) Isomer **8′**: ^1H NMR (C_6D_6, 20 °C) δ 1.10 (s, 6 H, CMe_2), 2.44 (d, 2 H, $^3J_{HH}$ = 1.9 Hz, CH_2), 3.56 (s, 3 H, CO_2Me), 6.10 (t, 1 H, $^3J_{HH}$ = 1.8 Hz, CH), 7.00−7.30 (m, 4 H, CH_{ar}); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 29.3 (s, C*Me*$_2$), 41.0 (*C*Me$_2$), 48.6 (CH_2), 52.5 (CO_2-Me), 110.8, 122.0, 127.3, 129.8, 131.4 (s, C_{ar}H, CH). EI−HRMS: *m*/*z* 216.1150, M$^+$ (exact mass calculated for $C_{14}H_{16}O_2$ 216.1150).

Synthesis of Pd[S(O$_2$)CH$_2$CMe$_2$-*o*-C$_6$H$_4$)(PMe$_3$)$_2$, 10. To a cooled (0 °C) solution of complex **2a** (0.18 g, 0.45 mmol) in 20 mL of toluene, 12 mL (0.45 mmol) of $SO_{2(g)}$ was added. The mixture was stirred at room temperature for 2 h and a white solid precipitated. The suspension was filtered and the solid, identified as compound **10**, dried under vacuum. The spectroscopic analysis of the mother liquor revealed the presence of a mixture of complexes **10** and **11**. Yield: 60%. Compound **10** can be purified by recrystallization from a mixture toluene:petrol ether (2:1).

Anal. Calcd for $C_{16}H_{30}O_2P_2SPd$: C, 42.2; H, 6.6. Found: C, 42.5; H, 6.7. IR (Nujol mull): 1146, 1064 cm^{-1} (υ (SO)). ^1H NMR (CD_2Cl_2, 20 °C) δ 1.15 (d, 9 H, $^2J_{HP}$ = 9.0 Hz, PMe_3), 1.43 (s, 3 H, CMe_2), 1.55 (d, 9 H, $^2J_{HP}$ = 8.3 Hz, PMe_3), 1.93 (s, 3 H, CMe_2), 2.35 (d, 1 H, $^3J_{HH}$ = 12.1 Hz, CH_2), 2.73 (d, 1 H, $^3J_{HH}$ = 12.1 Hz, CH_2), 6.90 (m, 1 H, CH_{ar}), 7.04 (m, 1 H, CH_{ar}), 7.26 (m, 1 H, CH_{ar}), 7.49 (m, 1 H, CH_{ar}); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) AX spin system, δ_A = −22.8, δ_X = −18.7, J_{AX} = 40.5 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 15.9 (d, $^1J_{CP}$ = 25 Hz, PMe_3), 16.1 (d, $^1J_{CP}$ = 21 Hz, PMe_3), 28.8 (s, C*Me*$_2$), 30.6 (s, C*Me*$_2$), 39.3 (d, $^4J_{CP}$ = 5 Hz, *C*Me$_2$), 76.1 (d, $^3J_{CP}$ = 11 Hz, CH_2), 123.8 (d, J_{CP} = 7 Hz, C_{ar}H), 124.4 (s, C_{ar}H), 124.8 (t, J_{CP} = 4 Hz, C_{ar}H), 135.0 (d, J_{CP} = 13 Hz, C_{ar}H), 148.5 (d, $^3J_{CP}$ = 3 Hz, C_{ar}), 154.7 (dd, $^2J_{CP}$ = 6 and 103 Hz, C_{ar}).

Synthesis of Pd[CH$_2$CMe$_2$C$_6$H$_4$-*o*-S(O$_2$)](PMe$_3$)$_2$, 11. A total of 0.16 mL (0.65 mmol) of $SO_{2(g)}$ was added to a cooled (0 °C) solution of complex **2a** (0.28 g, 0.65 mmol) in 40 mL of CH_2Cl_2. The solution turned yellow-orange and, after some minutes, colorless again. The mixture was stirred at this temperature for 4 h. The solvent was reduced under vacuum and the residue extracted with 20 mL of toluene. After filtration, partial evaporation of the solvent, addition of some petroleum ether, and cooling to −30 °C, compound **11** was isolated as white crystals in 92% yield. Anal. Calcd for $C_{16}H_{30}O_2P_2SPd$: C, 42.2; H, 6.6. Found: C, 42.3; H, 6.8. IR (Nujol mull): 1155, 1036 cm^{-1} (υ (SO)). ^1H NMR (CD_2Cl_2, 20 °C) δ 1.47 (d, 9 H, $^2J_{HP}$ = 8.6 Hz, PMe_3), 1.52 (s, 6 H, CMe_2), 1.54 (d, 9 H, $^2J_{HP}$ = 8.1 Hz, PMe_3), 1.88 (dd, 2 H, $^3J_{HP}$ = 5.7 and 10.7 Hz, CH_2), 7.29 (m, 2 H, CH_{ar}), 7.39 (m, 1 H, CH_{ar}), 7.95 (m, 1 H, CH_{ar}); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) AX spin system, δ_A = −24.3, δ_X = −16.1, J_{AX} = 39.7 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 15.6 (d, $^1J_{CP}$ = 25 Hz, PMe_3), 16.9 (d, $^1J_{CP}$ = 21 Hz, PMe_3), 34.8 (d, $^4J_{CP}$ = 8 Hz, C*Me*$_2$), 36.9 (d, $^2J_{CP}$ = 118 Hz, CH_2), 38.7 (s, *C*Me$_2$), 123.0, 125.2, 126.4, 129.2 (s, C_{ar}H), 147.6 (s, C_{ar}), 148.9 (d, $^3J_{CP}$ = 16 Hz, C_{ar}).

Synthesis of Pd{CH$_2$CMe$_2$C$_6$H$_4$-*o*-S(O$_2$)}(PMe$_3$)]$_2$, 12. Large colorless crystals of compound **12** were isolated after leaving a solution of complex **11** (0.26 g, 0.5 mmol) in MeOH (3 mL) exposed to air at

Table 1. Crystal and Refinement Data for Compounds **2a** and **10** and **12**

	2a	**10**	**12**
formula	$C_{16}H_{30}P_2Pd$	$C_{16}H_{30}O_2P_2PdS$	$C_{13}H_{21}O_2PPdS$
mol wt	390.76	454.82	378.74
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	P2/c (No. 15)
cell dimensions			
a, Å	9.331(3)	8.244(4)	13.490(6)
b, Å	16.349(1)	17.519(3)	11.841(5)
c, Å	12.628(3)	13.854(4)	19.602(6)
β, deg	93.90(2)	94.59(3)	103.79(3)
Z	4	4	8
V, Å^3	1922(1)	1994(1)	3040(3)
D_{calcd}, g cm^{-3}	1.350	1.515	1.654
F(*000*)	808	936	1536
temp, K	290	290	290
diffractometer	Rigaku AFC6S	Rigaku AFC6S	Rigaku AFC6S
radiation, λ Å	Cu Kα, 1.5418	Mo Kα, 0.7107	Mo Kα, 0.7107
μ, cm^{-1}	9.476	1.181	1.432
crystal size, mm	0.30 × 0.28 × 0.24	0.35 × 0.30 × 0.15	0.14 × 0.14 × 0.10
scan technique	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
decay, %	−10.00	−2.20	−0.93
transmision factors	0.788−1.000	0.949−1.000	0.923−1.000
scan speed (ω), deg min^{-1}	4	4	4
measured reflections	2978	3932	2961
observed reflections, I > 3σ(I)	1663	2234	1649
parameters	172	199	163
refln/parameter ratio	9.69	11.23	10.12
R^a	0.0716	0.0391	0.0356
R_w (w = σ_F^{-2})^b	0.0864	0.0452	0.0445
GOF	2.704	1.367	1.530
maximum Δ/σ in final cycle	0.2521	0.0004	0.1291
resd density (e Å^{-3})	+0.73, −0.91	+1.39, −0.61	+0.93, −0.77

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

room temperature for 2 days. Anal. Calcd for $C_{26}H_{42}O_4P_2S_2Pd_2$: C, 41.3; H, 5.5. Found: C, 41.4; H, 5.4. IR (Nujol mull): 1131 (υ (SO)$_{terminal}$), 1056 cm^{-1} (υ (SO)$_{bridging}$). ^{1}H NMR (CD_2Cl_2, 20 °C) δ 1.30 (d, 18 H, $^2J_{HP}$ = 9.6 Hz, PMe_3), 1.57 (s, 12 H, CMe_2), 1.99 (dd, 4 H, $^3J_{HP}$ = 8.7 Hz, CH_2), 7.35 (m, 4 H, CH_{ar}), 7.44 (m, 2 H, CH_{ar}), 7.91 (m, 2 H, CH_{ar}); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ -12.2 (s, PMe_3); ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C) δ 13.1 (d, $^1J_{CP}$ = 27 Hz, PMe_3), 29.6 (s, CH_2), 34.9 (s, C*Me*$_2$), 37.7 (s, *C*Me$_2$), 123.0, 126.8, 130.4 (s, $C_{ar}H$), 146.2, 147.6 (s, C_{ar}).

Reaction of Complex 11 with PMe_3. A suspension of complex **11** (0.40 g, 0.5 mmol) in 20 mL of MeOH was treated with 1 mL (1 mmol) of a 1 M solution of PMe_3 in THF. The mixture was stirred at room temperature for 2 h. The solvent was evaporated under reduced pressure and the solid residue dissolved in 10 mL of toluene. After partial concentration, addition of some petroleum ether and cooling to −30 °C provided compound **10** in quantitative yield.

NMR Study of the Reaction of the Metallacycle 2a with SO_2 at Low Temperature. Compound **2a** (0.022 g, 0.06 mmol) was dissolved in 0.6 mL of CD_2Cl_2 and NMR spectra were recorded at −80 °C (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}). $SO_{2(g)}$ (2.5 mL, 0.1 mmol) was added afterward at −90 °C and the initial colorless solution turned bright orange, NMR spectra were recorded again, starting at −80 °C and raising every 20 °C (−60 °C, −40 °C, −20 °C, 0 °C and 20 °C).

The same experiment was carried out in acetone-d_6 and toluene-d_8.

Selected NMR Data, −80 °C. (CD_2Cl_2): 2a, ^{1}H NMR δ 1.22 (s, 6 H, CMe_2), 1.69 (dd, 2 H, $^3J_{HP}$ = 5.6 and 8.3 Hz, CH_2); ^{31}P{^{1}H} NMR AX spin system, δ_A = −24.8, δ_X = −19.6, J_{AX} = 26 Hz; ^{13}C{^{1}H} NMR δ 35.2 (s, C*Me*$_2$), 52.1 (dd, $^2J_{CP}$ = 8 and 94 Hz, CH_2), 169.6 (dd, $^2J_{CP}$ = 13 and 121 Hz, C_{ar}). **9**, ^{1}H NMR δ 1.19 (bs, 6 H, CMe_2), 2.32 (dd, 2 H, $^3J_{HP}$ = 4.2 and 8.3 Hz, CH_2); ^{31}P{^{1}H} NMR AX spin system, δ_A = −25.8, δ_X = −16.8, J_{AX} = 31 Hz; ^{13}C{^{1}H} NMR δ 34.0 (bs, C*Me*$_2$), 62.2 (d, $^2J_{CP}$ = 83 Hz, CH_2), 169.1 (dd, $^3J_{CP}$ = 12 and 117 Hz, C_{ar}).

(Acetone-d_6): 2a, ^{1}H NMR δ 1.20 (s, 6 H, CMe_2), 1.66 (dd, 2 H, $^3J_{HP}$ = 5.9 and 8.1 Hz, CH_2); ^{31}P{^{1}H} NMR AX spin system, δ_A = −24.5, δ_X = −20.2, J_{AX} = 26 Hz; ^{13}C{^{1}H} NMR δ 35.8 (d, $^4J_{CP}$ = 6.4 Hz, C*Me*$_2$), 52.4 (dd, $^2J_{CP}$ = 8 and 95 Hz, CH_2), 170.4 (dd, $^2J_{CP}$ = 13 and 122 Hz, C_{ar}). **9**, ^{1}H NMR δ 1.16 (bs, 6 H, CMe_2), 2.32 (bt, 2 H, J_{app} = 4.3 Hz, CH_2); ^{31}P{^{1}H} NMR AX spin system, δ_A = −25.4, δ_X = −16.6, J_{AX} = 31 Hz; ^{13}C{^{1}H} NMR δ 34.4 (bs, C*Me*$_2$), 61.7 (dd, $^2J_{CP}$ = 7 and 89 Hz, CH_2), 169.5 (dd, $^3J_{CP}$ = 12 and 117 Hz, C_{ar}).

(Toluene-d_8): 2a, ^{1}H NMR δ 1.87 (s, 6 H, CMe_2), 2.18 (bt, 2 H, J_{app} = 6.5 Hz, CH_2); ^{31}P{^{1}H} NMR AX spin system, δ_A = −26.1, δ_X = −21.5, J_{AX} = 24 Hz; ^{13}C{^{1}H} NMR δ 35.9 (s, C*Me*$_2$), 52.7 (d, $^2J_{CP}$ = 87 Hz, CH_2), 169.7 (dd, $^2J_{CP}$ = 14 and 122 Hz, C_{ar}). **9**, ^{1}H NMR δ 1.46 (bs, 6 H, CMe_2), 2.51 (bs, 2 H, CH_2); ^{31}P{^{1}H} NMR AX spin system, δ_A = −26.7, δ_X = −18.6, J_{AX} = 30 Hz; ^{13}C{^{1}H} NMR δ 34.4 (bs, C*Me*$_2$), 59.4 (d, $^2J_{CP}$ = 84 Hz, CH_2), 167.8 (dd, $^3J_{CP}$ = 12 and 117 Hz, C_{ar}).

Synthesis of Pd[$CH_2CMe_2C_6H_4$-*o*-$S(O_2)$](dmpe), 13. To a solution of 0.24 g (0.7 mmol) of complex **2c** in 30 mL of toluene, cooled at 0 °C, 17 mL of $SO_{2(g)}$ (0.7 mmol) was added. The solution was stirred at this temperature for 3 h. During this time the color of the solution turned yellow and some white solid precipitated. The suspension was filtered, and the solid residue washed with Et_2O (2 × 5 mL) and dried. Complex **12** was crystallized from a mixture of toluene/petroleum ether (2:1) and isolated as white crystals in 72% yield. Anal. Calcd for $C_{16}H_{28}O_2P_2SPd$: C, 42.4; H, 6.2. Found: C, 42.0; H, 6.1. IR (Nujol mull): 1146, 1022 cm^{-1} (υ (SO)). ^{1}H NMR (CD_2Cl_2, 20 °C) δ 1.50 (d, 6 H, $^2J_{HP}$ = 10.0 Hz, PMe_2), 1.52 (s, 6 H, CMe_2), 1.61 (d, 6 H, $^2J_{HP}$ = 10.0 Hz, PMe_2), 1.69−2.07 (m, 4 H, P−CH_2), 1.75 (dd, 2 H, $^3J_{HP}$ = 6.0 and 9.0 Hz, CH_2), 7.29 (m, 2 H, CH_{ar}), 7.43 (m, 1 H, CH_{ar}), 7.99 (m, 1 H, CH_{ar}); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) AX spin system, δ_A = 22.6, δ_X = 24.0, J_{AX} = 24.7 Hz; ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C) δ 11.3 (d, $^1J_{CP}$ = 26 Hz, PMe_2), 12.3 (d, $^1J_{CP}$ = 21 Hz, PMe_2), 25.9 (dd, $^1J_{CP}$ = 28 Hz, $^2J_{CP}$ = 13 Hz, P−CH_2), 28.9 (dd, $^1J_{CP}$ = 31 Hz, $^2J_{CP}$ = 20 Hz, P−CH_2), 34.3 (d, $^2J_{CP}$ = 85 Hz, CH_2), 35.7 (d, $^4J_{CP}$ = 8 Hz, C*Me*$_2$), 36.5 (s, *C*Me$_2$), 123.0, 126.0, 126.2, 129.2 (s, $C_{ar}H$), 147.9 (s, C_{ar}), 149.1 (d, $^3J_{CP}$ = 17 Hz, C_{ar}).

X-ray Structure Determination of Compounds 2a, 10, and 12. Crystals of the appropriate size were mounted on a glass fiber and transferred to an AFC6S-Rigaku automatic diffractometer. Accurate unit cell parameters and an orientation matrix were determined in each

Table 2. Crystal and Refinement Data for Compound **2b**

	2b
formula	$C_{18}H_{24}Pd$
mol wt	346.77
crystal system	orthorhombic
space group	P *bca*
cell dimensions, *a*, Å	19.908(5)
b, Å	10.311(4)
c, Å	14.735(5)
$\alpha = \beta = \gamma$ (deg)	90
Z	8
V, Å^3	3025(2)
D_{calcd}, g cm^{-3}	1.523
F(000)	1424
Temp, K	293
diffractometer	Siemens AED
radiation, λ Å	0.71073
μ, cm^{-1}	12.12
crystal size, mm	0.21 × 0.32 × 0.28
scan technique	$\omega/2\theta$
measured reflections	4458
observed reflections	2982
parameters	179
extinction coefficient	0.0019(4)
final *R* indices, [$I > 2\sigma(I)$]	R1[a] = 0.0423, wR2[b] = 0.1214
R indices (all data)	R1[a] = 0.0613, wR2[b] = 0.1303

[a] $R1 = \sum|F_o - F_c|/\sum(F_o)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^2$.

Table 3. Selected Bond Distances and Angles for Compound **2a**

Bond Distances (Å)			
Pd−P1	2.310(4)	C1−C2	1.54(2)
Pd−P2	2.341(3)	C2−C5	1.51(2)
Pd−C1	2.08(1)	C5−C6	1.39(2)
Pd−C6	2.04(1)		
Bond Angles (deg)			
P1−Pd−P2	98.3(1)	Pd−C1−C2	108.0(8)
P1−Pd−C1	90.4(3)	C1−C2−C5	103.0(1)
P2−Pd−C6	94.6(4)	C2−C5−C6	116.0(1)
C1−Pd−C6	77.4(5)	Pd−C6−C5	115.1(8)

case by least-squares fitting from the settings of 25 high-angle reflections. Crystal data and details on data collection and refinements are given in Table 1. Data were collected by the $\omega/2\theta$ scan method. Lorentz and polarization corrections were applied. Decay was monitored by measuring three standard reflections every 200 measurements. Decay and semiempirical absorption corrections (ψ method) were also applied. The structure was solved in each case by Patterson methods and subsequent expansion of the model using DIRDIF.[25] Reflections having $I > 3\sigma(I)$ were used for structure refinement. All non-hydrogen atoms were anisotropically refined by full-matrix least. The hydrogen atoms were localized in difference electron density maps or included at idealized positions with fixed isotropic displacements parameters 1.2 times the value of their parent atom. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[26] software system and ORTEP[27] for plotting.

X-ray Structure Determination of Compound 2b. The intensity data of **2b** were collected at room temperature on a Siemens AED single-crystal diffractometer using a graphite monochromated Mo Kα radiation and the $\omega/2\theta$ scan technique. Crystallographic and experimental details for the structures are summarized in Table 2.

A correction for absorption was made (maximum and minimum values for the transmission coefficient were 1.000 and 0.436).[28]

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) (SHELX-97)[29] first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms.

The hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms. In the final cycles of refinement, a weighting scheme for **2b** was $w = 1/[\sigma^2F_o^2 + (0.0887\ P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ was used.

Table 4. Selected Bond Distances and Angles for Compound **10**

Bond Distances (Å)			
Pd−S	2.298(2)	S−O2	1.457(6)
Pd−P1	2.317(2)	S−C1	1.809(7)
Pd−P2	2.367(2)	C(1)−C(2)	1.53(1)
Pd−C(10)	2.053(6)	C(2)−C(5)	1.554(9)
S−O1	1.474(5)	C(5)−C(10)	1.399(8)
Bond Angles (deg)			
S−Pd−P2	89.80(7)	O1−S−O2	114.0(4)
S−Pd−C10	85.9(2)	S−C1−C2	119.4(4)
P1−Pd−P2	96.91(7)	C1−C2−C5	107.3(5)
P1−Pd−C10	88.7(2)	C2−C5−C10	119.6(6)
Pd−S−C1	108.6(2)	Pd−C10−C5	126.4(5)

Table 5. Selected Bond Distances and Angles for compound **12**

Bond Distances (Å)			
Pd1−S	2.281(2)	S−O2	1.499(5)
Pd1−P1	2.296(2)	S−C10	1.800(7)
Pd1−O2	2.175(5)	C1−C2	1.53(1)
Pd1−C1	2.033(8)	C2−C5	1.54(1)
S−O1	1.462(5)	C5−C10	1.39(1)
Bond Angles (deg)			
S−Pd1−O2	89.4(1)	O1−S−O2	110.7(3)
S−Pd1−C1	87.6(2)	Pd1−O2−S	124.4(3)
P1−Pd1−O2	93.6(1)	Pd1−C1−C2	116.9(5)
P1−Pd1−C1	89.2(2)	C1−C2−C5	113.0(6)
Pd1−S−O2	111.4(2)	C2−C5−C10	123.4(6)
Pd1−S−C10	114.8(2)	S−C10−C5	125.2(5)

Table 6. Selected Bond Distances and Angles for Compound **2b**

Bond Distances (Å)			
Pd1−C1	2.023(3)	C1−C6	1.405(4)
Pd1−C10	2.030(3)	C6−C7	1.500(4)
Pd1−C11	2.342(4)	C7−C10	1.528(5)
Pd1−C12	2.319(4)	C11−C12	1.348(6)
Pd1−C15	2.311(3)	C15−C16	1.344(5)
Pd1−C16	2.276(4)		
Bond Angles (deg)			
C1−Pd1−C10	79.08(13)	C12−Pd1−C11	33.63(14)
C10−Pd1−C16	95.39(14)	C6−C1−Pd1	115.7(2)
C10−Pd1−C15	96.86(14)	C1−C6−C7	115.4(3)
C16−Pd1−C15	34.07(13)	C6−C7−C10	104.7(3)
C1−Pd1−C12	99.30(13)	C7−C10−Pd1	112.0(2)
C1−Pd1−C11	102.24(13)		

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond lengths and angles for **2a**, **2b**, **10**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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