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# Binuclear Complexes of Bis-Chelating Ligands Based on [1,4]Dioxocino[6,5-*b*:7,8-*b*′]dipyridine Moieties

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Ligands based on a [1,4]dioxocino[6,5-*b*:7,8-*b*′]dipyridine (**doxpy**) core were prepared and characterized. They all present two equal chelating moieties each one including one N, O, or S donor in addition to a pyridinic nitrogen. These ligands displayed high selectivity for the formation of binuclear complexes. At least one $d^8$ ion ($Pd^{II}$ or $Pt^{II}$) complex was prepared for each type of ligand. The stereochemical behavior of the ligands is discussed on the basis of NMR spectra. Stable atropoisomers were obtained in the case of N-oxides or in case chiral centers were introduced in the ethereal bridge. As for the complexes, stable enantiomers appear to be in principle attainable for all the new compounds. A test on the cooperative ability of two $Pd^{II}$ centers has been grounded on the microstructure of the styrene/CO copolymer catalytically produced by a binuclear pyridine-imino complex. In fact, comparison with the microstructure of the copolymers produced by related single-site mono- and (open-chain) binuclear catalysts reveals significant difference, thus giving indication of possible synergic metal activity.

## Introduction

Studies of bimetal complexes as promoters of useful reactions are not only prompted as logical extension of the huge amount of information gained on single-site metal activity but also suggested by the structure and performance of important enzymes.[1] This area has been the object of many discussions.[2] We wish only to remark that the unequivocal assessment of cooperative effects from the two metal centers requires satisfactory insight into both the single-site and the related bimetal mechanisms. Homogeneous comparison of the results obtained from experiments carried out in strictly similar conditions on these two different types of catalysts can provide indication of synergy.

Given these considerations, we undertook the synthesis of a new class of ligands having structural features proper to exhibit bis-chelating ability, while keeping the two metal centers within a definite distance range suited for reciprocal interaction between their separate coordination spheres.[3]

More precisely, the ligands reported in this study are binucleating molecules basically of the general type illustrated in Figure 1, where **X** is a donor function supported by the **f** group. These dioxocino-dipyridine derivatives are in short indicated as **doxpy-2fX**.

Their design was suggested by the following main considerations. First, the choice of a bipyridine core for the ligands is in keeping with the well-established versatile coordinative ability of bidentate chelating N-heterocycles.[4] It is also required that the ligand favors a controlled and tunable proximity of the two metal centers by avoiding both excess of rigidity and access to conformations with M−M distances that are too long. In **doxpy-2fX** molecules, the **fX** branches are held by two rigid supports, each including one donor, which can rotate in a restricted range of reciprocal orientations. This control of the geometry also precludes that the ligand behaves as tetradentate toward a single metal center, as generally observed in related systems lacking the ethereal bridge.[5]

Finally, more impetus to the investigation on these ligand systems stems from the interest for asymmetric catalysis.[6] As for the free ligands, stereogenic centers can be introduced in various positions to achieve stable chirality. In the absence of them or of steric hindrance to the rotation around the Cpy-Cpy bond, isomerization could occur at room temperature, in which case the compounds have to be considered prochiral

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(1) Ringe, D.; Petsko, G. A.; Desmarais, W.; Holz, R. C. *Abstracts of Papers*, 222nd American Chemical Society National Meeting, Chicago, IL, U.S.A., August 26−30, 2001, INOR-194.
(2) For example, see: van den Beuken, E. K.; Feringa, B. L. *Tetrahedron* **1998**, *54*, 12985.
(3) Panunzi, A.; De Felice, V.; Fraldi, N.; Roviello, G.; Ruffo, F. *Inorg. Chem. Commun.* **2005**, *8*, 1049.
(4) Reedijk, J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; Vol. 73.
(5) Constable, E. C.; Elder, S. M.; Healy, J.; Ward, M. D.; Tocher, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 4590.
(6) Shibasaki, M.; Matsunaga, S.; Kumagai, N. *Synlett* **2008**, *11*, 1583.


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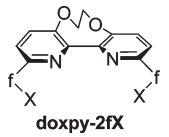

doxpy-2fX

**Figure 1.** General formula of ligands of type **doxpy-2fX**.

species. On the other hand, because of the atropoisomerism, their complexes are reasonably expected to be chiral and configurationally stable.

In a preliminary communication[3] we described the preparation of one ligand (**fX**: CH=N-*p*-tolyl) and of one related $Pd^{II}$ binuclear complex, also characterized by solid state structure determination. Herein, we report results about the preparation and characterization of a family of **doxpy-2fX** type ligands, whose chelating moieties bear, beside the pyridinic nitrogen, another nitrogen, oxygen, or sulfur donor in the **X** function. Several $Pd^{II}$ or $Pt^{II}$ complexes are described, along with results on chirality features of ligands and complexes. One promising preliminary test deals with the cooperative ability seemingly displayed by a Pd(II) complex in promoting styrene/CO copolymerization catalysis.

## Results and Discussion

**Synthesis of Ligands.** The key precursor of all the new species is **doxpy-2Me**,[3] which has been prepared in good yields according to Scheme 1.

Starting from this compound, the other functionalized derivatives can be obtained according to the synthetic pathways described in Scheme 2.

Oxidation of the dimethyl compound **doxpy-2Me** with $KMnO_4$ affords the dicarboxylic acid **doxpy-2CO$_2$H** in good yield. This is transformed with oxalyl chloride into the corresponding chloride that by methanol treatment yields the diester **doxpy-2CO$_2$Me**, and finally is reduced to the dialcohol **doxpy-2CH$_2$OH**.

Although the latter compound is already a potential ligand, it mainly attracts interest as a suitable intermediate for the preparation of the disulfide **doxpy-2CH$_2$SPh** as well as of the dibromomethyl derivative **doxpy-2CH$_2$Br**, and thus for the attainment of the diamine **doxpy-2CH$_2$NMe$_2$**.

On the other hand, **doxpy-2CH$_2$OH** can be favorably used by reaction with active $MnO_2$ for the synthesis of the dialdheyde **doxpy-2CHO**, which has been obtained in the preliminary work[3] in low yield (16%) directly from **doxpy-2Me**.

Comparative copolymerization experiments (see below) required the use of the analogous not-coupled versions (**nc-2fx**) of the **doxpy-2fx** type molecules. In the absence of the Cpy-Cpy coupling, the yields by using the synthetic approach of Scheme 2 were, however, unsatisfactory in contrast with those attained by the procedure shown in Scheme 3, which involves the preparation of Npy-oxide derivatives.

It should be noted that the corresponding coupled N-oxides attract direct interest for the expected high steric hindrance to interconversion between atropoisomers by rotation about the C−C bond, as discussed below. Furthermore, they also offer competitive alternative pathways for the early reaction steps in Scheme 2 (particularly for the preparation of **doxpy-2CH$_2$OH**, according to Scheme 4).

**Complexes.** Binuclear complexes were prepared and characterized for each type of ligand (Scheme 5).

The syntheses followed protocols suggested by those reported for related single-metal species. The NMR spectra of the complexes gave evidence that all the new compounds are binuclear, as found for the diimine Pd(II) derivative described in the preliminary work.[3] In all but the dichloro-species, the complexes could in principle display *cis-trans* isomerism within each metal coordination sphere. Actually, as inferred by the pattern of their NMR spectra, they were found to adopt a unique configuration in solution. This has been clearly shown in Scheme 5 when assessed, in some cases, by analogy with mononuclear complexes.

The diimine $Pd^{II}$ complexes [(PdClMe)$_2$(**doxpy2CH=NEt**)] (**Pd1**) and [(PdClMe)$_2$(**nc2CH=NEt**)] (**Pd2**) were prepared by reacting the appropriate ligand with a suitable mononuclear species, as shown for the coupled ligand in eq 1. In the case of **Pd1**, the configuration was inferred from that of the closely related compound [(PdClMe)$_2$(**doxpy-2CH=NC$_6$H$_4$Me**].[3]

A similar procedure afforded the analogous mononuclear palladium complex [(PdClMe{(5-MeO)-py-2-CH=NEt)}] (**Pd3**). The three corresponding cationic complexes, respectively **Pd4**, **Pd5**, and [(PdMe(MeCN)-{(5-MeO)-py-2-CH=NEt)}]$BF_4$ (**Pd6**), used for the comparative copolymerization tests, are generated by use of $AgBF_4$, as shown for the product containing the coupled ligand in eqs 2 and 3.

By analogy with the known synthesis[7,8] of simple mononuclear related complexes, the disulfide was reacted with [PdClMe(1,5-COD)], resulting in the formation of the binuclear species **Pd6** (eq 4).

The diamino derivative **doxpy-2CH$_2$NMe$_2$** was coordinated by reaction with a bis-phenoxide precursor (eq 5).[9] The phenate complex appeared difficult to handle and was transformed into [(PdCl$_2$)$_2$(**doxpy-2CH$_2$NMe$_2$**)] (**Pd7**) by treatment with HCl(g) in methylene chloride.

Finally, the two platinum carboxylate complexes **Pt1** and **Pt2** could be obtained as exemplified in eq 6 by adapting a known procedure.[10a] The configuration of the complexes was attributed on the basis of that of the related mononuclear complexes [PtMe(picolinate)-(Me$_2$S)][10a] and [PtCl(8-hq)(tht)][10b] (8-Hhq = 8-hydroxyquinaldine).

**Stereochemistry of Ligands and Complexes.** Atropoisomerism is the basic feature that may give rise to optical isomers for ligands of type **doxpy-2fX** and their binuclear complexes. However, it should be noted that in absence of stereogenic centers (e.g., in the ethereal bridge or in the groups **X** and/or **f**), stable atropoisomers are expected only if co-planarity of the two rings is forbidden;

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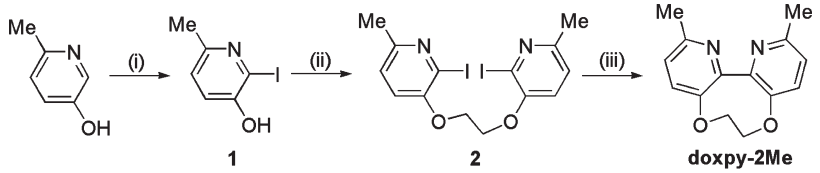
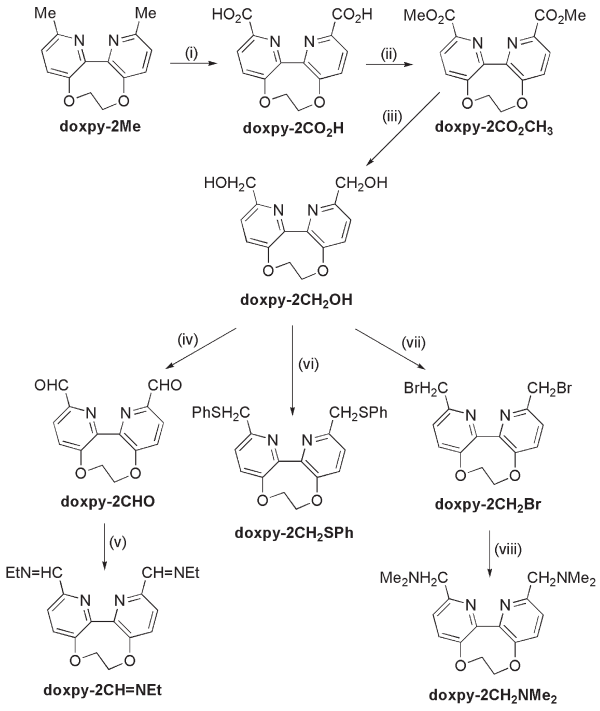
(9) Kapteijn, M. G.; Grove, M. D.; Kooijman, H.; Smeets, J. J. W.; Spek, L. A.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 526.
(10) (a) Ziatdinov, V. R.; Oxgaard, J.; Mironov, O. A.; Young, K. J. H.; Goddard, W. A.III; Perlana, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 7404. (b) Yue, C.; Jiang, F.; Xu, Y.; Yuan, D.; Chen, L.; Yan, C.; Hong, M. *Cryst. Growth Des.* **2008**, *8*, 2721.

**Scheme 1.** Synthesis of **doxpy-2Me** According to Reference 3



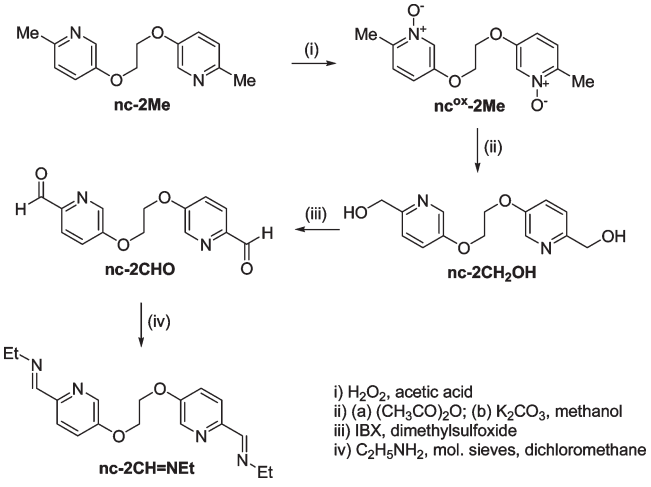

i) $I_2$, $NaHCO_3$, THF/water; ii) $(CH_2OTf)_2$, NaH, DMF; iii) $NiCl_2{\cdot}6H_2O$, $PPh_3$, Zn, DMF

**Scheme 2.** Synthesis of the New Ligands



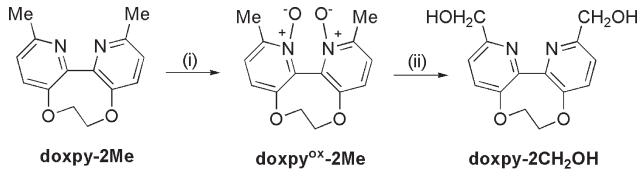

i) $KMnO_4$, water; ii) (a) $COCl_2$, dichloromethane; (b) MeONa, methanol; iii) $NaBH_4$, methanol; iv) IBX, DMSO; v) $C_2H_5NH_2$, mol. sieves, dichloromethane; vi) (a) $MeSO_2Cl$, $Et_3N$, THF; (b) PhSNa, ethanol; vii) $PBr_3$, dichloromethane; viii) $Me_2NH$, ethanol

**Scheme 3.** Synthesis of Ligands **nc-2CH=NEt**




i) $H_2O_2$, acetic acid
ii) (a) $(CH_3CO)_2O$; (b) $K_2CO_3$, methanol
iii) IBX, dimethylsulfoxide
iv) $C_2H_5NH_2$, mol. sieves, dichloromethane

**Scheme 4.** Alternative Pathway for the Synthesis of **doxpy-2CH$_2$OH**




i) $H_2O_2$, acetic acid; ii) (a) $(CH_3CO)_2O$; (b) $K_2CO_3$, methanol

otherwise, the ligands have to be considered as simply prochiral.

Information on the interconversion between atropoisomers in ligands (Scheme 6) is offered by the signal of $OCH_2$ protons in the $^1$H NMR spectra (Figure 2). In fact, if rotation is slow (in the NMR time scale) the two diastereotopic protons on each carbon atom (a and b in Scheme 6 for **doxpy-2Me**) are expected to be not equivalent, thus giving rise to an AA′XX′ system (actually, two apparent doublets were generally observed). On the other hand, fast interconversion, which involves passage through co-planar arrangement of the two rings, would make them chemically equivalent.

Fast interconversion is observed for all ligands here reported, as well as for the precursor **doxpy-2Me**. Some influence of the solvent is observed, for example, in the latter case the signal in dmso-$d_6$ is broader than in chloroform at room temperature. However, moderate temperature increase until 323 K already determines fast interconversion on the NMR time scale.

Substantial stop to the inversion could in principle arise from hindrance to the required conformational changes of the 9-membered ring including the $(CH_2O-)_2$ chain. However, from previous studies on related compounds,[11] this is not expected to be a determining factor at room temperature.

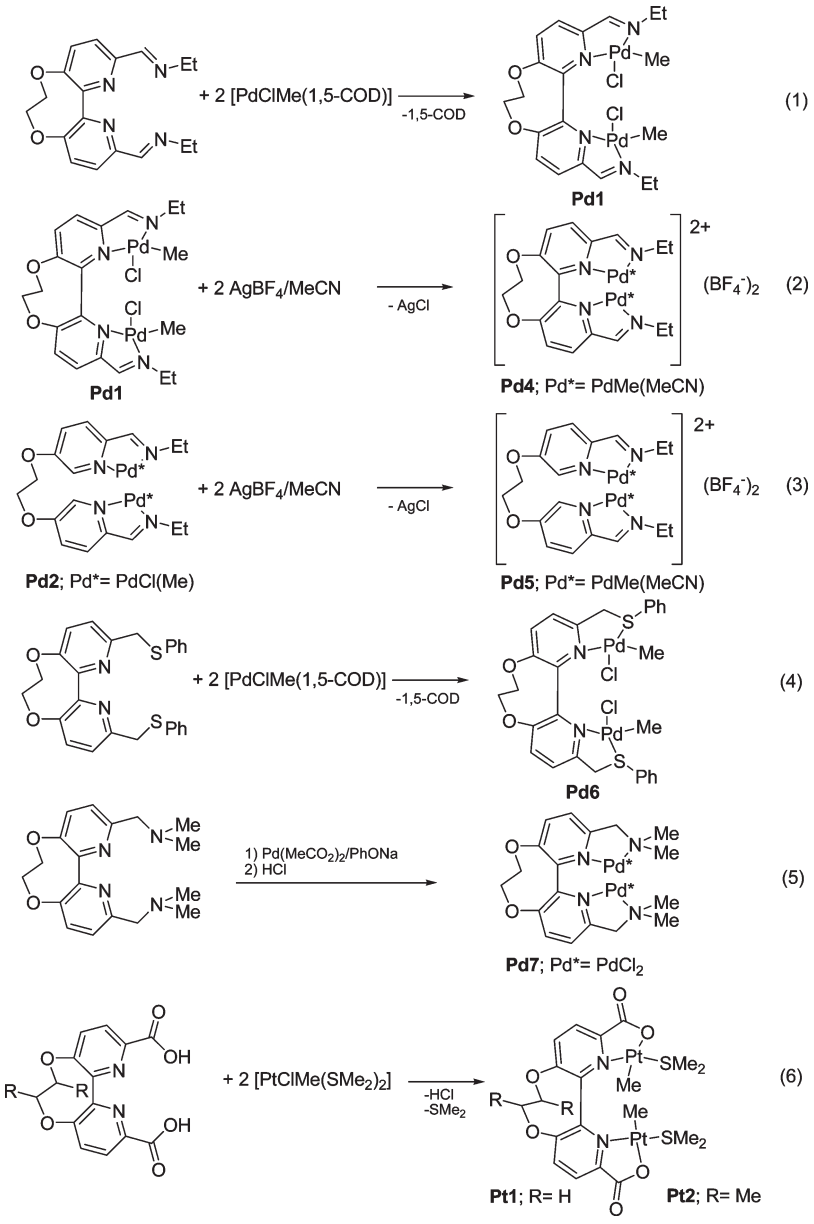
On the other hand, inversion could be hindered in case the two **X** groups are suited to interact reciprocally or with the opposite nitrogen. It is noteworthy that the $OCH_2$ signal is particularly broad in the case of the dialcohol and of the dicarboxylic ligand.

Inversion could be easily blocked by rigid bonding of one or more atoms to the pyridinic nitrogen atoms. As expected, the two $OCH_2$ protons signals in **doxpy$^{ox}$-2Me** are apparent doublets, thus giving evidence of hindered (possibly blocked) inversion.

As for the complexes, although the type of coordination sphere should be specifically considered in each case, it is expected that a most important and plausibly sufficient obstruction to inversion should be determined by the mutual hindrance of the two coordinated metal fragments. In fact, for all the complexes the multiplicity of the signal of the $OCH_2$ protons (apparent doublets, e.g., Figure 3) confirmed the expected lack of isomerization.

(11) (a) Rashidi-Ranjbar, P.; Sandstrom, J. *Tetrahedron Lett.* **1987**, *28*, 1537. (b) Rashidi-Ranjbar, P.; Najafpour, J.; Piri, F. *J. Phys. Org. Chem.* **1998**, *11*, 781.

**Scheme 5.** Synthesis and Structure of the Complexes




As noted before, another approach to configurationally stable chiral ligands can be based on the introduction of chiral stereogenic centers (Scheme 7). A previous report,[12] claiming that the chiral bridge −OCH(Me)CH(Me)O− stereospecifically induces atropoisomerism in molecules with the same [1,4]dioxocino[6,5-*b*:7,8-*b*′]dipyridine core, prompted us to introduce this enantiomerically pure sequence with reaction conditions and workup similar to those adopted for dimethylene bridged molecules (Scheme 5).

In fact, the NMR pattern of the Me protons of the bridge points to the presence of only one detectable diastereomer for **Medoxpy-2CO$_2$H**. This is plausibly the thermodynamically stable species in equilibrium with the minor abundant one through the free rotation around the C−C bond.

Two diastereomers in 2:1 ratio are instead observed for the corresponding complex [{PtMe(SMe$_2$)}$_2$(**Medoxpy-2CO$_2$**)]. In this case the diastereomeric ratio is reasonably controlled by the kinetics of their formation because in this case the rotation is expected to be hindered.

**X-ray Molecular Structure of [(PdClMe)$_2$(doxpy-2CH$_2$SPh)] (Pd6).** Yellow crystals of [(PdClMe)$_2$(**doxpy-2CH$_2$SPh**)] were grown by slow evaporation of solvent from a methanol solution of the complex. The X-ray molecular structure (Figure 4) discloses a moderate tetrahedral distortion of the square planar Pd environment from the mean plane (a factor affecting reactivity in related mononuclear species).[7] Only one geometrical isomer is present, that is, with a *trans* Npy-Pd-Me arrangement. The same feature was observed in the related mononuclear complex.[8]

The distances of S1, N1, Cl1, C14, Pd1 from the mean least-squares plane of coordination are −0.098(1), 0.049(2), −0.091(1), 0.043(2), 0.097(1) Å (for S1′, N1′,

(12) Milani, B.; Alessio, E.; Mestroni, G.; Zangrando, E.; Randaccio, L.; Consiglio, G. *J. Chem. Soc., Dalton Trans.* **1996**, 1021.

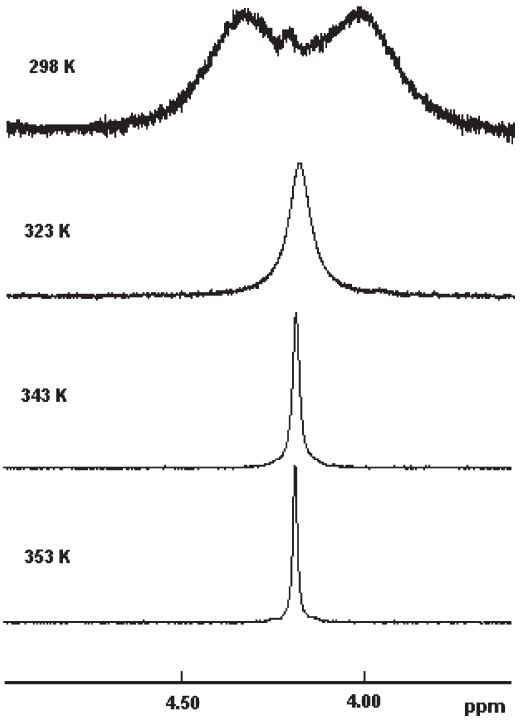
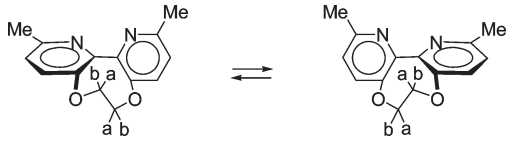



**Figure 2.** $^1$H NMR spectra ($OCH_2$ region) of **doxpy-2Me** in dmso-$d_6$ at various temperatures.

**Scheme 6.** Interconversion between Atropisomers of **doxpy-2Me**



Cl1′, C14′, Pd1′ are respectively 0.133(1), −0.084(2), 0.123(1), −0.080(2), −0.092(1) Å).

It should be noted that also in solution, one single diastereomer (actually a couple of enantiomers) with $C_2$ symmetry was observed in the $^1$H NMR spectrum at room temperature. In this compound the sulfur atom is configurationally stable, as indicated by the presence of two doublets accounting for the diastereotopic $CH_2S$ protons.

Comparison with the previously determined[3] structure of [(PdClMe)$_2$(**doxpy-2CH=NC$_6$H$_4$Me**)] shows that the two molecules contain the same coordinated fragment {PdMeCl}, with Me *trans* to the pyridinic nitrogen. It can be observed that, notwithstanding the different nature and hybridization of the atoms in the **f-X** branch, the two structures are strictly comparable, thus confirming the versatile ability of the **doxpy** core to afford binucleating functions.

The intramolecular distance of the two metals in [(PdClMe)$_2$(**doxpy-2CH$_2$SPh**)] is 3.2449(5) and in [(PdClMe)$_2$(**doxpy-2CH=NC$_6$H$_4$Me**)] is 3.3807(5) Å.

The angle between the two mean coordination planes in the two complexes is significantly different. In fact, it is 37.5(1)° in [(PdClMe)$_2$(**doxpy-2CH=NC$_6$H$_4$Me**)] and 16.2(1)° in [(PdClMe)$_2$(**doxpy-2CH$_2$SPh**)].

**Synergy.** As a preliminary investigation, the catalytic properties of the binuclear complex [{PdMe(MeCN)}$_2$-(**doxpy-2CH=NEt**)](BF$_4$)$_2$ (**Pd4**) have been tested in CO/styrene copolymerization. Its performance has been compared to those of the corresponding mononuclear and binuclear open-chain species, namely, [(PdMe(MeCN){(**5-MeO)-py-2-CH=NEt**)}]BF$_4$ (**Pd6**) and [{PdMe(MeCN)}$_2$(**nc-2CH=NEt**)](BF$_4$)$_2$ (**Pd5**).

The performance of the three catalysts is substantially different, as indicated by the microstructure of the copolymers determined by comparison of their carbon spectra with literature data[13] (Figure 5 shows the relevant methylene region). In particular, the mononuclear catalyst

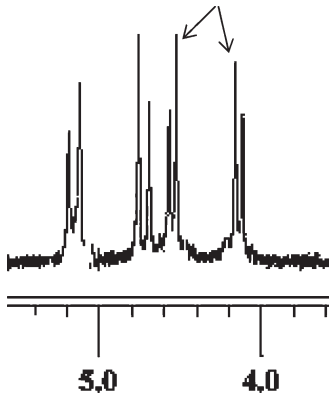



**Figure 3.** Apparent doublets accounting for the $-OCH_2CH_2O-$ protons in complex **Pd6** (pointed out by the arrows). The other two doublets account for the $-CH_2SPh$ protons.

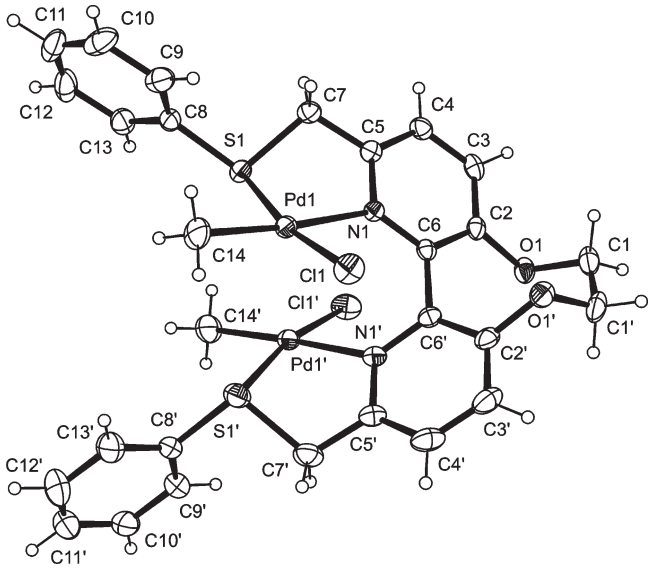



**Figure 4.** Ortep view of [(PdClMe)$_2$(**doxpy-2CH$_2$SPh**)]. Thermal ellipsoids are drawn at 30% probability level. Selected bond distances (Å) and angles (deg): Pd1−N1 2.220(3), Pd1−S1 = 2.283(1), Pd1−Cl1 = 2.322(1), Pd1−C14 = 2.025(4), S1−C7 = 1.833(4), Pd1′−N1′ = 2.189(3), Pd1′−S1′ = 2.280(1), Pd1′−Cl1′ = 2.324(1), Pd1′−C14′ = 2.019(4), S1′−C7′ = 1.838(5); N1−Pd1−S1 = 78.22(8), S1−Pd1−C14 = 96.7(1), C14−Pd1−Cl1 = 88.3(1), Cl1−Pd1−N1 = 96.4(8), Pd1−S1−C7 = 90.3(1), Pd1−S1−C8 = 117.0(1), C7−S1−C8 = 102.9(2), N1′−Pd1′−S1′ = 79.77(8), S1′−Pd1′−C14′ = 95.4(1), C14′−Pd1′−Cl1′ = 88.5(1), Cl1′−Pd1′−N1′ = 96.19(8), Pd1′−S1′−C7′ = 91.8(4), Pd1′−S1′−C8′ = 114.1(1), C7′−S1′−C8′ = 102.7(2); N1−C6−C6′−N1′ = 49.2(4), Pd1−N1−C5−C7 = −7.5(3), Pd1−S1−C7−C5 = ¬58.0(2), N1−Pd1−S1−C7 = −45.5(1), C7−S1−C8−C9 = −60.5(4), Pd1′−N1′−C5′−C7′ = −5.7(4), Pd1′−S1′−C7′−C5′ = 52.9(3), N1′−Pd1′−S1′−C7′ = −41.1(1), C7′−S1′−C8′−C9′ = −55.1(4).

(13) (a) Barsacchi, M.; Batistini, A.; Consiglio, G.; Suter, U. W. *Macromoelcules* **1992**, *25*, 3604. (b) Yuan, G.-C.; Lu, S.-J. *Tetrahedron Lett.* **2001**, *42*, 4069.

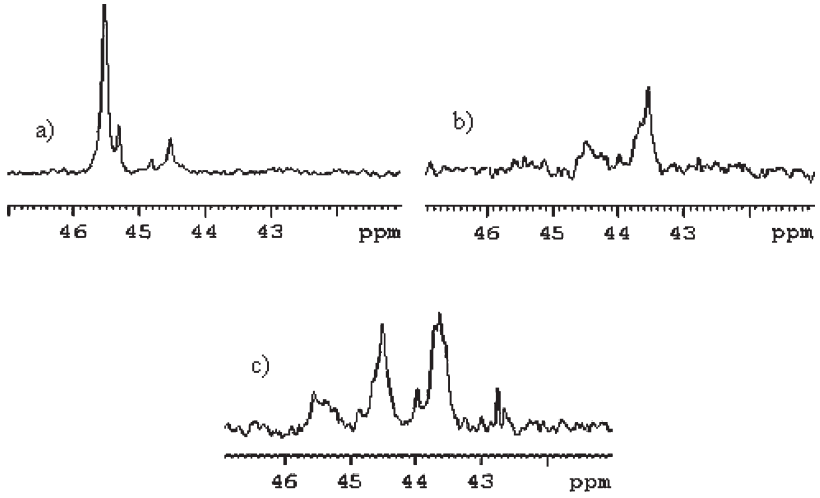
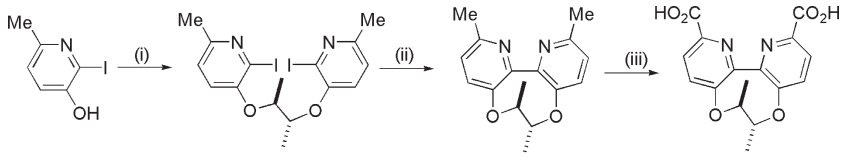



**Figure 5.** Methylene region of the $^{13}C$ NMR spectra of the copolymers obtained respectively with [{PdMe(MeCN)}$_2$(**doxpy-2CH=NEt**)](BF$_4$)$_2$ (a), [{PdMe(MeCN)}$_2$(**nc-2CH=NEt**)](BF$_4$)$_2$ (b), and [(PdMe(MeCN){(**5-MeO)-py-2-CH=NEt**)}]BF$_4$ (c).

**Scheme 7.** Synthesis of the Chiral Ligand **Medoxpy-2CO$_2$H**




i) (CHMeOTf)$_2$, NaH, DMF; ii) Ni(PPh$_3$)$_4$, Zn, DMF; iii) KMnO$_4$, water

favors the attainment of an atactic polymer, while the open-chain derivative promotes a significant degree of syndiotacticity. This latter result is in agreement with that obtained by using a comparable dinuclear Pd complex with a linear bridge.[14]

In a quite uncommon way for this type of binuclear catalysts,[14] complex [{PdMe(MeCN)}$_2$(**doxpy-2CH=NEt**)](BF$_4$)$_2$ affords the copolymer with a considerable level of isotacticity. This result, which should be compared with the previous study[14] on related systems, suggests that the expected synergic activity between the two metal centers plausibly exists.

For sake of completeness, it must be recalled that Pd complexes with hindered diimine ligands favor the formation of isotactic copolymers.[15]

## Conclusion

This work demonstrates that binucleating ligands based on a [1,4]dioxocino[6,5-*b*:7,8-*b*′]dipyridine (**doxpy**) scaffold are able to keep two metal centers within a controlled range of distances, in principle suited for promoting synergic activity. The versatility of this new class of ligands has been revealed by associating the pyridine function of each chelating moiety to another donor group (alcolate, carboxylate, sulphide, imine, amine), and representative neutral or cationic binuclear complexes of Pd$^{II}$ and Pt$^{II}$ have been easily attained for each ligand.

According to the expectation, a preliminary test on the cooperative ability of two Pd$^{II}$ centers in the catalyzed copolymerization of styrene/CO suggests the occurrence of significant synergic metal activity. Future work will explore the mechanistic origin of this effect. Catalytic tests will be also extended to other processes, aiming to disclose and utilize synergy within a wide range of reactions promoted by both homo- and heterobinuclear **doxpy**-derived complexes.

## Experimental Section

Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk techniques. All solvents were reagent grade, and, if necessary, were purified by standard methods. All other chemicals were used as received from commercial vendors. The NMR spectra ($^1H$ for all the compound and $^{13}C$ for relevant species) were recorded on Varian XL 200 MHz and Gemini 300 MHz instruments. $^1H$ [$^{13}C$] chemical shifts are referenced using the residual solvent peak at $\delta$ 7.26 [77.0] for $CDCl_3$, 2.49 [39.4] for dmso-$d_6$, and 2.05 [20.8] for acetone-$d_6$. Routine coupling constants are not listed. For describing multiplicities the following abbreviations were used: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; app, apparent; m, multiplet; br, broad. The synthesis and the characterization of the ligands is reported in the Supporting Information

**Preparation of [(PdClMe)$_2$(doxpy-2CH=NEt)] (Pd1), [(PdClMe)$_2$(nc-2CH=NEt)] (Pd2), [PdClMe{(5-MeO)-py-2-CH=NEt)}] (Pd3).** The three imine neutral complexes were prepared by the same general procedure. To the stirred suspension of [(PdClMe)$_2$($\mu$-SMe$_2$)$_2$] (0.088 g, 0.20 mmol) in dichloromethane (2.5 mL) was added dropwise a stoichiometric amount of imine dissolved in 2 mL of the same solvent. The resulting orange mixture was stirred at room temperature for 6 h. After

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concentration in vacuo to 1 mL, addition of diethyl ether afforded precipitation of a dark yellow solid that was recovered and dried (yield: 70−80%).

**[(PdClMe)$_2$(doxpy-2CH=NEt)]**, $^1$H NMR ($CDCl_3$): $\delta$ 8.42 (s, 2H, N=CH), 7.69 (d, 2H, H4 and H9, $^3J_{H4-H3}$ = 8.4 Hz), 7.64 (d, 2H, H3 and H10), 4.66 (app d, 2H, $^2J$H-H = 9.6 Hz, −OC*H*HC*H*HO−), 4.14 (app d, 2H, −OCH*H*CH*H*O−), 3.95 (m, 2H, NC*H*H), 3.72 (m, 2H, NCH*H*), 1.65 (t, 6H, $^3J$H-H = 7.2 Hz, Me), 1.05 (s. 6H, Pd-Me); Elemental analysis: calcd (%) for $C_{20}H_{26}Cl_2N_4O_2Pd_2$: C 37.64, H 4.11, N 8.78. Found: C 37.80, H 4.19, N 8.55.**[(PdClMe)$_2$(nc-2CH=NEt)]**, $^1$H NMR ($CDCl_3$): $\delta$ 8.61 (s, 2H), 8.27 (d, 2H), 7.64 (dd, 4H), 4.58 (br, 4H, $OCH_2$), 3.81 (q, 4H, $NCH_2$), 1.37 (t, 6H, Me), 0.99 (s, 6H, Pd-Me); Elemental analysis: calcd (%) for $C_{20}H_{28}Cl_2N_4O_2Pd_2$: C 37.52, H 4.41, N 8.75. Found: C 37.78, H 4.35, N 8.91. **[PdClMe{(5-MeO)-py-2-CH=NEt)}]**, $^1$H NMR ($CDCl_3$): $\delta$ 8.76 (d, 1H), 8.23 (s, 1H), 7.59 (d, 1H, $^3J$H-H = 9.0 Hz), 7.35 (dd, 1H, $^3J$H-H = 9 Hz, $^4J$H-H = 3.2 Hz), 3.97 (s, 3H, OMe), 3.79 (dd, 1H, $^3J$H-H = 7.2 Hz, $^4J$H-H = 1.9 Hz, $NCH_2$), 1.36 (t, 3H, Me), 1.00 (s, 3H, Pd-Me). Elemental analysis: calcd (%) for $C_{10}H_{15}ClN_2OPd$: C 37.40, H 4.71, N 8.72. Found: C 37.72, H 4.88, N 8.96.

**Preparation of [{PdMe(MeCN)}$_2$(doxpy-2CH=NEt)](BF$_4$)$_2$ (Pd4), [{PdMe(MeCN)}$_2$(nc-2CH=NEt)](BF$_4$)$_2$ (Pd5), [PdMe(MeCN){(5-MeO)-py-2-CH=NEt)}]BF$_4$ (Pd6).** The three imine cationic complexes were prepared by the same general procedure. To a stirred suspension of the neutral precursor (0.20 mmol of Pd atoms) in dry acetonitrile (2.5 mL) was added dropwise at 0 °C stoichiometric silver tetrafluoroborate (0.038 g, 0.20 mmol) dissolved in 2 mL of the same solvent. The orange color faded to light yellow while the mixture was stirred at room temperature for 15 min. After removal of the white precipitate the solvent was evaporated in vacuo to afford the complex in satisfactorily pure form.

**[{PdMe(MeCN)}$_2$(doxpy-2CH=NEt)](BF$_4$)$_2$**, $^1$H NMR ($CD_3CN$): $\delta$ 8.73 (s, 2H, CH=N), 8.20 (ABq, $^3J$H-H = 8.4 Hz, 4H, H3, H4,H9, and H10), 4.75 (app d, 2H, $^2J$H-H = 9.0 Hz, OC*H*HC*H*HO), 4.30 (app d, 2H, OCH*H*CH*H*O), 3.80 (m, 4H, $NCH_2$), 1.38 (t, 6H, $^3J$H-H = 6.8 Hz, Me), 1.04 (s, 6H, Pd-Me); Elemental analysis: calcd (%) for $C_{24}H_{32}B_2F_8N_6O_2Pd_2$: C 35.03, H 3.92, N 10.21. Found: C 34.81, H 3.94, N 9.98. **[{PdMe(MeCN)}$_2$(nc-2CH=NEt)](BF$_4$)$_2$**, $^1$H NMR ($CD_3CN$): $\delta$ 8.41 (s, 2H, CH=N), 8.18 (s, 2H), 7.90 (d, 2H, $^3J$H-H = 8.8 Hz), 7.71 (d, 2H), 4.58 (s, 4H, $OCH_2$), 3.67 (q, 4H, $^3J$H-H=7.4 Hz, $CH_2CH_3$), 1.26 (t, 6H, Me), 0.94 (s, 6H, Pd-Me); Elemental analysis: calcd (%) for $C_{24}H_{34}B_2F_8N_6O_2Pd_2$: C 34.94, H 4.15, N 10.19. Found: C 34.63, H 4.27, N 10.38. **[PdMe(MeCN){(5-MeO)-py-2-CH=NEt)}](BF$_4$)**, $^1$H NMR ($CD_3CN$): $\delta$ 8.39 (s, 1H, CH=N), 8.20 (d, H6, 1H, $^4J_{H6-H4}$ = 2.6 Hz), 7.85 (d, 1H, H3, $^3J_{H3-H4}$ = 8.4 Hz), 7.61 (dd, 1H, H4), 3.96 (s, 1H, OMe), 3.67 (q, 2H, $^3J$H-H = 6.8 Hz, $CH_2CH_3$), 1.25 (t, 3H, $^3J$H-H = 6.8 Hz, Me), 0.93 (s, 3H, Pd-Me). Elemental analysis: calcd (%) for $C_{12}H_{18}BF_4N_3OPd$: C 34.85, H 4.39, N 10.16. Found: C 34.66, H 4.51, N 10.40.

**Preparation of [{PtMe(SMe$_2$)}$_2$(doxpy-2CO$_2$)] (Pt1) and [{PtMe(SMe$_2$)}$_2$(Medoxpy-2CO$_2$)] (Pt2).** To the stirred suspension of [PtClMe($SMe_2$)$_2$] (0.037 g, 0.10 mmol) in dichloromethane (2.5 mL) was added dropwise a solution of a stoichiometric amount of the sodium salt of the suited acid (0.050 mmol) dissolved in 2 mL of methanol. The resulting orange mixture was stirred at room temperature for 6 h. Slow addition of diethyl ether afforded the products as yellow-orange powders (yield: 60−70%).

**[{PtMe(SMe$_2$)}$_2$(doxpy-2CO$_2$)]**, $^1$H NMR ($CDCl_3$): $\delta$ 8.41 (ABq, 4H, H3, H4, H9, and H10), 4.86 (app d, $^2J$H-H = 10 Hz, 2H, OC*H*HC*H*HO), 4.46 (d, 2H, OCH*H*CH*H*O), 2.55 (s, 12H, $Me_2S$), 1.40 (s, $^3J$Pt-H = 78 Hz, 6H, Pt-Me); Elemental analysis: calcd (%) for $C_{20}H_{26}N_2O_6Pt_2S_2$: C 28.44, H 3.10, N 3.32. Found: C 28.34, H 3.21, N 3.23. **[{PtMe(SMe$_2$)}$_2$(Medoxpy-2CO$_2$)]**, $^1$H NMR ($CDCl_3$): more abundant isomer, $\delta$ 8.42 (ABq, 4H, H3, H4, H9, and H10), 4.42 (m, 2H, OCH), 2.39 (s, 12H, $Me_2S$), 1.68 (d, $^3J$H-H =7.5 Hz, 6H, Me), 1.27 (s, $^3J$Pt-H = 80 Hz, 6H, Pt-Me); less abundant isomer, $\delta$ 8.45 (d, 2H, H4, and H9), 8.33 (d, 2H, H3, and H10), 4.43 (m, 2H, OCH), 2.71 (s, 12H, $Me_2S$), 1.70 (d, $^3J$H-H = 6.0 Hz, 6H, Me), 1.22 (s, $^3J$Pt-H = 79 Hz, 6H, Pt-Me). Elemental analysis: calcd (%) for $C_{22}H_{30}N_2O_6Pt_2S_2$: C 30.28, H 3.46, N 3.21. Found: C 30.35, H 3.09, N 3.33.

**Table 1.** Crystal, Collection, and Refinement Data for [(PdClMe)$_2$(**doxpy-2CH$_2$SPh**)]

| | |
|---|---|
| formula | $C_{28}H_{28}N_2O_2Cl_2S_2Pd_2$ |
| fw | 772.34 |
| size (mm) | 0.50×0.45×0.35 |
| color | yellow |
| cryst syst | monoclinic |
| $T$ (K) | 295 |
| space group | $P2_1/c$ |
| $a$ (Å) | 17.6561(9) |
| $b$ (Å) | 11.285(1) |
| $c$ (Å) | 14.767(2) |
| α (deg) | 90 |
| $\beta$ (deg) | 98.346(6) |
| $\gamma$ (deg) | 90 |
| $V$ (Å$^3$) | 2911.2(5) |
| $Z$ | 4 |
| $D_c$ (g cm$^{-3}$) | 1.762 |
| $\mu$ (mm$^{-1}$) | 1.592 |
| $F$(000) | 1536 |
| $\theta_{max}$ (deg) | 27.50 |
| no. of measd reflns | 31208 |
| no. of indep reflns | 6614 [$R$(int) = 0.0772] |
| no. of obs reflns [$I > 2\sigma(I)$] | 4174 |
| no. of params | 345 |
| $R_1$; $wR_2$ [I > 2σ(I)] | 0.0360; 0.0630 |
| $R_1$; $wR_2$ (all data) | 0.0880; 0.0743 |
| $\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.476; −0.406 |

**Preparation of [(PdClMe)$_2$(doxpy-2CH$_2$SPh)].** To a stirred solution of **doxpy-2CH$_2$SPh** (0.0172 g, 0.039 mmol) in chloroform (2 mL) was added dropwise a solution of [PdClMe(1,5-COD)] (0.020 g, 0.076 mmol) in the same solvent (2 mL). The orange solution was stirred for 0.5 h at room temperature. The volume was reduced in vacuo to 1 mL, and diethyl ether was added to precipitate the product (yield: 85%).

$^1$H NMR ($CDCl_3$), $\delta$ 7.92 (m, 4H), 7.58 (ABq, 4H, H3, H4, H9, and H10), 7.44 (m, 6H), 5.15 (d, 2H, $^2J$H-H = 14 Hz, SC*H*H), 4.72 (d, 2H, SCH*H*), 4.54 (app d, 2H, $^2J$H-H = 8.6 Hz, OC*H*HC*H*HO), 4.13 (d, 2H, OCH*H*CH*H*O), 0.80 (s, 6H, Pd-Me). Elemental analysis: calcd (%) for $C_{28}H_{28}Cl_2N_2O_2Pd_2S_2$: C 43.54, H 3.65, N 3.63. Found: C 43.88, H 3.47, N 3.82.

**Preparation of [(PdCl$_2$)$_2$(doxpy-2CH$_2$NMe$_2$)].** A solution of **doxpy-2CH$_2$NMe$_2$** (0.028 g, 0.085 mmol), [$Pd(AcO)_2$] (0.037 g, 0.17 mmol), and PhONa (0.038 g, 0.33 mmol) in dichloromethane (5 mL) was stirred for 20 h at room temperature. Addition of diethyl ether caused formation of a precipitate, which resulted in difficult purification. Hence, the solid was dissolved in the minimum amount of dichloromethane and treated with excess gaseous HCl. After 1 h an excess of LiCl was added, and the solvent was removed in vacuo. The product was washed with cold water, acetone, and dried in vacuo (yield: 85%).

$^1$H NMR (dmso-$d_6$): $\delta$ 8.14 (d, 2H, H4 and H9, $^3J_{H4-H3}$, = 8.0 Hz), 7.88 (d, 2H, H3 and H10), 4.58 (app d, 4H, $^2J$H-H = 14.0 Hz, $CH_2N$), 4.34 (app t, 4H, $^2J$H-H = 4.0 Hz, −$OCH_2CH_2O$−), 2.94 (s, 12H, $NMe_2$). Elemental analysis: calcd (%) for $C_{18}H_{24}Cl_4N_4O_2Pd_2$: C 31.65, H 3.54, N 8.20. Found: C 32.03, H 3.70, N 8.06.

**CO-Styrene Polymerization Catalyzed by [{PdMe(MeCN)}$_2$(doxpy-2CH=NEt)](BF$_4$)$_2$ (Pd4), [{PdMe(MeCN)}$_2$(nc-2CH=NEt)](BF$_4$)$_2$ (Pd5), and [PdMe(MeCN){(5-MeO)-py-2-CH=NEt)}](BF$_4$) (Pd6).** The appropriate cationic Pd catalyst (0.10 mmol) was

suspended in 6 mL of freshly distilled styrene. After stirring for 5 min, CO was bubbled in the system, and the resulting solution was kept under CO atmosphere for 14 h. The reaction mixture was then filtered through Celite, and the volume of the solution was reduced in vacuo. Addition of methanol caused precipitation of the white polymer (0.12 g from **Pd4**, 0.43 g from **Pd5**, and 0.17 g from **Pd6**).

**Determination of the X-ray Molecular Structure of [(PdClMe)$_2$(doxpy-2CH$_2$SPh)].** Crystal data and collection details for [(PdClMe)$_2$(**doxpy-2CH$_2$SPh**)] are given in Table 1. The most relevant bond distances and angles are reported in the caption of Figure 4. Data collection was performed at 295 K on a Bruker-Nonius KappaCCD single crystal diffractometer with monochromated Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation. Data were collected and integrated using the Bruker Nonius COLLECT software package,[16] and a semiempirical absorption correction was applied (multiscan SADABS).[17] The structure was solved by direct methods and refined by the full matrix least-squares method on $F^2$ against all independent measured reflections (SHELX-97 package).[18] All non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were placed in idealized positions and refined by a riding model with thermal parameters $U_{iso}$ set to the $U_{eq}$ of the carrier atooms. For the graphical representation, ORTEP-III for Windows was used as implemented in the program system WinGX.[19]

All crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC). Deposition number is CCDC 708822. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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**Supporting Information Available:** Analytical and spectral characterization data of the new ligands (9 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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