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Roof-Shaped Halide-Bridged Bimetallic Complexes via Ring Expansion Reaction

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Binucleating behavior of rigid triptycene-based ligands has been studied. It has been demonstrated that trans-spanned transition-metal mononuclear complexes bearing 1,8-bis(diisopropylphosphino)triptycene (L1) and 1-diisopropylphosphino-8-diphenylphosphinotriptycene (L2) react with an appropriate transition-metal precursor via a ring-expansion pathway to form unusual bimetallic quasi-closed structures. New palladium and rhodium complexes featuring strongly bent (ca. 115°) $M_2(\mu\text{-}Cl_2)$ cores with very closely spanned metal centers (less than 3 Å) have been prepared using the described ring-expansion reaction and have been fully characterized. Despite a constrained arrangement of the binuclear system, halogen bridges in all new compounds were stable in both the solid state and solution showing no tendency for dissociation even in the presence of added Lewis bases. Spontaneous resolution of the dissymmetric $Pd_2(\mu\text{-}Cl)_2Cl_2$(1-diisopropylphosphino-8-diphenylphosphinotriptycene) (**2**) into enantiopure antipodes is discussed as well.

Introduction

The synthesis of structurally defined polymetallic complexes is a great challenge in inorganic and organometallic chemistry due to their potential use as enzyme-mimicking[1] and conventional[2] catalysts, new materials,[3] and pharmaceuticals.[4] Complexes featuring potentially “communicating” short-bridged polymetallic structures are of particular interest, because of a possible cooperation between the metals that often finds an expression in unique physical and chemical properties.[5] Clearly, the better “communication” can be achieved when a $M_2(\mu\text{-}X_2)$ core exists in the face-to face (Figure 1a) or strongly bent bridged forms (e.g., Figures 1b−d where the $M_1X_1X_2$ and $M_2X_1X_2$ interplanar angle is lower than 160°), so that axial orbitals of the metal centers converge in the space produced by X−M−X planes.

Lately, a variety of edge-sharing d^8 [$M_2(\mu\text{-}X_2)X_2L_2$] complexes have been prepared.[6] Although a majority of structurally characterized bimetallic compounds of this type possess a planar $M_2(\mu\text{-}X_2)$ core, examples of the bent bimetallic units are known in the literature.[7]

General trends in the formation of such butterfly-like dimeric compounds (Figure 1b) and factors governing the spontaneous bending have been studied theoretically and

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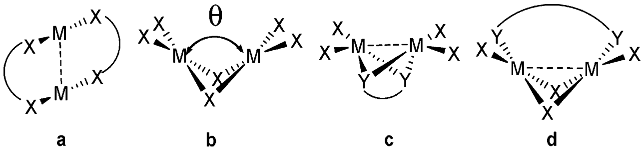
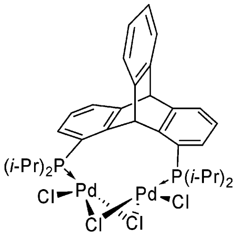


Figure 1. Possible modes of communicating metal centers.

have been well-reviewed by Aullón et al.[8,9] However, their synthesis is often fortuitous.

"Sterically induced bending" (Figure 1c), which appears a more rational strategy to the synthesis of closely bridged bimetallic complexes, was recently documented.[9] For example, roof-shaped alkyldithiolato-[10] or alkyldiphosphido-bridged[11] binuclear complexes have been prepared and characterized. In these cases, the presence of the alkyl linker enforces them sterically to adopt the desired conformation.

Another possible route for the construction of the desired bent structures, which also may be classified as "sterically enforced" bending, could be the utilization of a somewhat rigid ligand bearing adequately remote donor groups and capable of binucleation (as represented in Figure 1d). For instance, a class of trans-chelating ligands (TransPhos, SpanPhos, etc.)[12] may be seen as suitable candidates. However, only a limited number of structurally characterized bimetallic compounds (almost exclusively of rhodium)[13] exemplify this approach. With regard to dipalladium complexes, only two structures where a bidentate ligand *sterically* enforces the $Pd_2(\mu\text{-}X_2)$ unit to adopt a bent conformation have been previously reported. Guzei et al. reported that 1,3-bis(3,5-dialkylpyrazolyl-1-carbonyl)benzenes form the corresponding $[Pd_2(\mu\text{-}Cl_2)Cl_2L^\frown L]$ compounds featuring a $Pd_2(\mu\text{-}Cl_2)$ interplanar angle of ca. 138° and a metal−metal separation of ca. 3.21 Å.[14] Similar parameters have been previously observed by Hambley et al. for 1,5-bis{*o*-(*p*-toluenesulfinyl)phenoxy}-3-oxapentane complexes.[15] To the best of our knowledge, Pd_2X_2 rhombuses in other structurally defined ligand-bridged compounds of this type (Figure 1d) are planar or only slightly distorted from planarity.[16]



1

Figure 2. Structure of **1**.

Recently, we reported about the isolation and characterization of an unusual quasi-closed chloride-bridged dipalladium complex **1** bearing a strongly curved 1,8-bis(diisopropylphosphino)triptycene ligand (L1; Figure 2).[17a] We found that the Pd_2Cl_4 core is bent (ca. 122°) and the corresponding $Pd\cdots Pd$ distance is as short as 3.036 Å. On the other hand, incorporation of the Pd_2Cl_4 unit between the phosphine donors results in a significant increase in the $P\cdots P$ distance (5.907 Å). This becomes possible owing to a drastic deviation of the phosphine groups from the planes of the corresponding aromatic rings (planarity deviation is ca. 0.54 Å) at the expense of an increased strain in the 10-membered ring.

A priori, because the observed intermetallic distance in **1** is short, a cooperative effect between the two metal centers may be anticipated if applied as a catalyst. The monoligated quasi-closed structure may also provide an unrivaled opportunity to create a sterically less-demanding active bimetallic site (for example, in comparison to a majority of doubly ligated A-frame complexes).[18] Finally, an undersaturated (intrinsically reactive) catalyst or catalyst precursor may form owing to the unique ligation mode.

Although, in our early communication, we reported that complex **1** could be isolated from a ring-expansion reaction of the corresponding monometallic palladium precursor (Scheme 1),[17a] other aspects of its formation, properties, and stability, as well as the possibility to apply the described

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(16) On the basis of the search within Cambridge Structural Database (CSD version 5.27 with May 2006 updates), only two bent complexes could be found that correspond to a *monoligated* $Pd_2(\mu\text{-}X_2)X_2L^\frown L$ structure (refs 14 and 15). Examples of the flat complexes of this type can be found in: (a) Smith, D. C., Jr.; Gray, G. M. *Chem. Commun.* **1998**, 2771. (b) Garcia-Anton, J.; Pons, J.; Solans, X.; Font-Bardia, Me.; Ros, J. *Eur. J. Inorg.Chem.* **2002**, *12*, 3319. (c) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **2002**, *41*, 1036. (d) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **2002**, *338*, 219. (e) Pamplin, C. B.; Rettig, S. J.; Patrick, B. O.; James, B. R. *Inorg. Chem.* **2003**, *42*, 4117. (f) Smith, D. C., Jr.; Lake, C. H.; Gray, G. M. *Dalton Trans.* **2003**, *14*, 2950.

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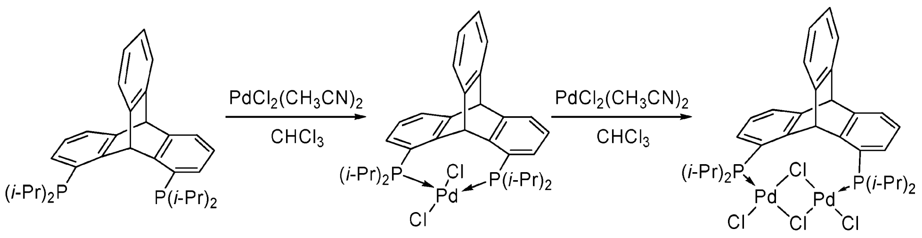
Scheme 1. Synthesis of **1** by the Ring-Expansion Reaction



L1 **PdCl$_2$L1** **1**

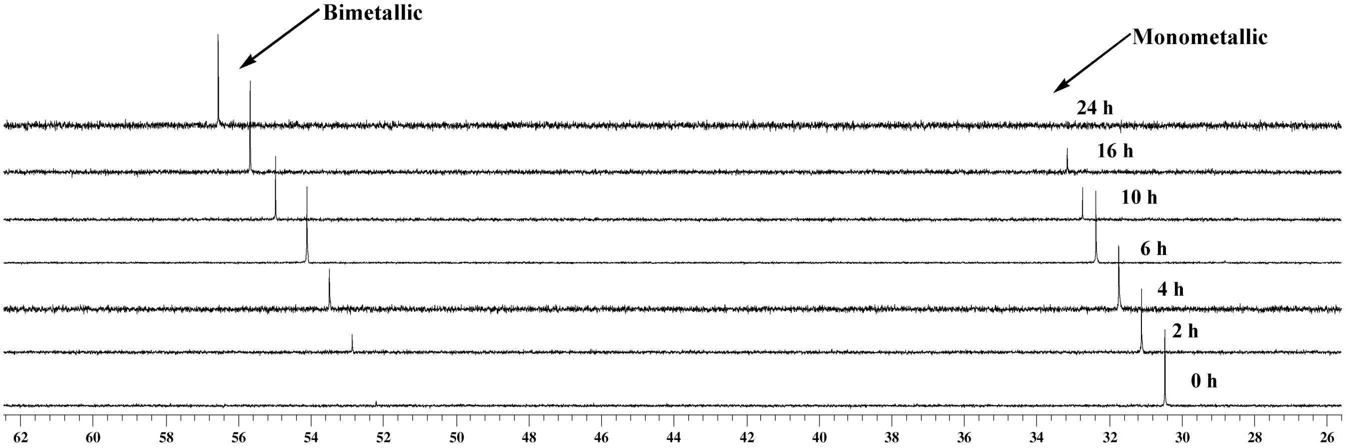


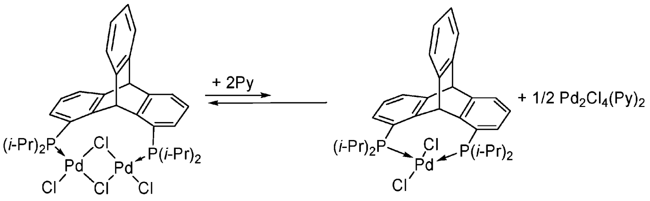
Figure 3. ^{31}P NMR changes during the formation of **1** by the ring expansion.

ring expansion to the synthesis of other bimetallic compounds, were not clear. In the present report, we wish to address these issues.

Results and Discussion

Stability of [Pd$_2$(μ-Cl$_2$)Cl$_2$-(1,8-Bis(diisopropylphosphino)triptycene)] (1). Taking into account the constrained and visually unfavorable arrangement of the bimetallic complex **1**, we initially attributed its formation to the difference in solubility between the monometallic precursor (highly soluble) and the bimetallic product (sparingly soluble). If indeed this were the case, the formation of such bimetallic complexes would be questionable under high-dilution conditions and **1** could remain just a chemical curiosity. To test the stability of the bent structure, the reaction between the *trans*-[1,8-bis(diisopropylphosphino)triptycene]palladium dichloride (PdCl$_2$L1) and one additional equivalent of the palladium dichloride bis-acetonitrile complex (Scheme 1) was performed under high-dilution conditions and was followed by ^{31}P{^{1}H} NMR. Fortunately, the conversion of the monometallic palladium precursor into **1** was clean and quantitative at 45 °C over 24 h: a singlet ascribed to the monometallic *trans*-PdCl$_2$L1 (33.6 ppm) was gradually transformed into a singlet centered at 56.4 ppm, which is attributed to **1** (Figure 3). No formation of byproducts was observed either by ^{31}P or ^{1}H NMR.

Scheme 2. Equilibrium between the Monometallic and the Bimetallic Complexes



Because, as we reported earlier,[17a] the monometallic precursor exhibited an exceptional stability in both the solid state and solution in the absence of an excessive palladium chloride (no equilibrium processes have been observed by ^{31}P{^{1}H} NMR at various temperatures), the complex **1** possessing the bent μ-chloride bridged bimetallic core is likely to form because of the thermodynamic stability of the bridge despite a conformational tension in the spanning ligand.

Curiously, we found that the affinity of L1 to palladium is so high that it is capable of scavenging palladium salts from solutions containing other metals. For instance, if $^1/_2$ equivalent of L1 is added to the chloroform solution of NiCl$_2$(diglyme), PdCl$_2$(CH$_3$CN)$_2$, and PtCl$_2$(CH$_3$CN)$_2$, a yellow precipitate of **1** forms after ca. 24 h at 45 °C. On the basis of the weight of the isolated **1**, we were able to remove 84% of the initial palladium loading from the original solution.

The relative stability of the bimetallic core was tested using the reaction of **1** with pyridine. Previously, we showed that, upon dissolution of **1** in coordinating solvents (DMSO, THF, etc.), the parent monometallic *trans*-PdCl$_2$L1 formed quantitatively. However, when 2 equiv of pyridine were added to the chloroform solution of **1**, no significant changes in the ^{31}P{^{1}H} NMR spectrum were observed. The disintegration of the chloride bridge was very sluggish, even after 4 h at room temperature; though, it can be completed upon the addition of larger quantities of pyridine (100-fold excess) and a prolonged reaction time (12 h) (Scheme 2). Interestingly, the only observable signal detected by ^{31}P{^{1}H} NMR

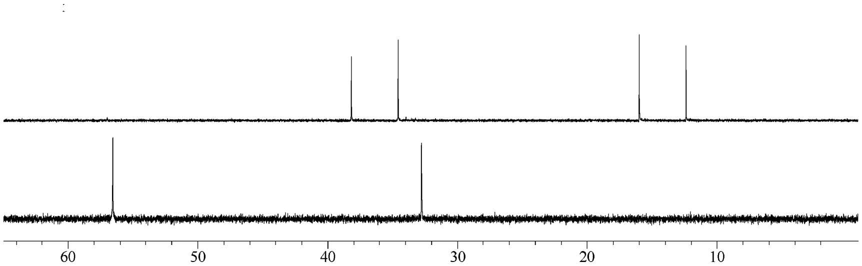
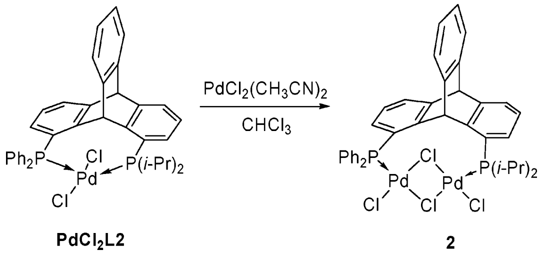


Figure 4. Synthesis of **2** by the ring expansion: $^{31}P\{^1H\}$ NMR spectra of *trans*-$PdCl_2(L2)$ (top) and **2** (bottom).

Scheme 3. Synthesis of **2** by the Ring-Expansion Reaction



was attributed to the monometallic *trans*-$PdCl_2L1$ complex. These results suggest that L1 has a very good donor ability forming very stable binuclear complexes.

Synthesis and Characterization of the New [$M_2(\mu$-$Cl_2)$-Cl_2L] Complexes. The stability exhibited by **1** inspired us to apply the described ring-expansion reaction to the synthesis of other bimetallic complexes. Initially, we attempted to employ a dissymmetric 1-diisopropylphosphino-8-diphenylphosphinotriptycene (L2) to bridge between metal centers (expectantly, in their bent form).

As in the previous example, we prepared the ligand using our published procedure[17a] and allowed it to react with a stoichiometric amount of $PdCl_2(CH_3CN)_2$ in deuterated chloroform at room temperature, resulting in the formation of the corresponding monometallic *trans*-$PdCl_2(L2)$ complex quantitatively as was confirmed by $^{31}P\{^1H\}$ NMR measurements [the complex exhibits a characteristic AB pattern due to the coupling established by two different phosphorus nuclei coordinated to the same Pd center (38.06 and 14.47 ppm, $J_{P-P} = 576$ Hz)[17a]]. Then, an additional 1 equiv of $PdCl_2(CH_3CN)_2$ was added, and the progress of the reaction described by Scheme 3 was followed by $^{31}P\{^1H\}$ NMR. As in the aforementioned entry, the gradual formation of the new material was observed (Figure 4).

The $^{31}P\{^1H\}$ NMR spectrum of the new product displayed two sharp singlets with resonance frequencies of 32.74 and 56.54 ppm. By analogy with **1** (Figure 3), the low-field shift of the signals relative to the monometallic complex could indicate the formation of the desired bimetallic compound. The absence of phosphorus−phosphorus coupling also confirms the structure—different phosphine groups do not chelate the same palladium center.

Suitable single crystals of **2**, grown by slow evaporation of the saturated chloroform solution at room temperature, were subjected to X-ray diffraction analysis to verify the structure. We found that the resulting compound indeed possesses the roof-shaped $Pd_2(\mu$-$Cl)_2Cl_2$ core. The crystallographic parameters are presented in Table 1.

Although the environment around each of the palladium atoms is only slightly distorted from the square-planar geometry with bond angles ranging within 84.37° and 94.62°, the bimetallic rhombus is bent: the Pd(1)−Cl(1)−Cl(2) and Pd(2)−Cl(1)−Cl(2) interplanar angle was calculated as 116.15°, and the Pd(1)−Pd(2) separation is as short as 2.969 Å (Figure 5). Both of these parameters are even smaller than those observed previously in **1**. The yet stronger twist in this case is likely due to a slightly different trans influence by electronically dissymmetric donor phosphine groups. For example, the Pd(2)−Cl(1) bond (trans to the better σ-donor group—dialkylphosphine) is longer than the corresponding Pd(1)−Cl(2) bond (trans to the diarylphosphine group), 2.406 Å versus 2.386, while the Pd(1)−Cl(2) and Pd(2)−Cl(2) bonds are essentially equal (2.330 and 2.335 Å). Remarkably, the incorporation of a Pd_2Cl_4 fragment between the phosphine donors results in a significant increase in the P···P distance

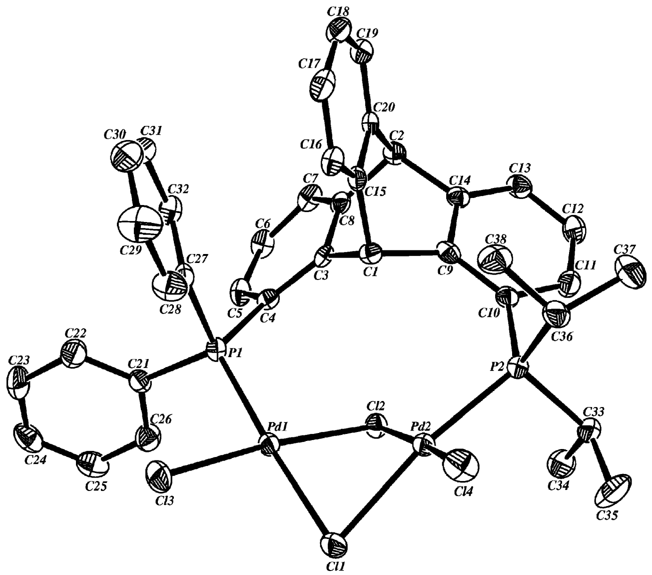


Figure 5. ORTEP drawing (50% probability ellipsoids) of the representative enantiomer of **2**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cl(1)−Pd(1) 2.3860(8), Cl(1)−Pd(2) 2.4062(8), Cl(2)−Pd(2) 2.3302(8), Cl(2)−Pd(1) 2.3344(8), Cl(3)−Pd(1) 2.2837(8), Cl(4)−Pd(2) 2.2821(9), P(1)−Pd(1) 2.2179(8), P(2)−Pd(2) 2.2302(8), Pd(1)−Pd(2) 2.9687(4), C(4)−P(1) 1.821(3), C(10)−P(2) 1.838(3); P(1)−Pd(1)−Cl(3) 89.11(3), P(1)−Pd(1)−Cl(2) 94.62(3), Cl(3)−Pd(1)−Cl(2) 173.84(3), P(1)−Pd(1)−Cl(1) 175.15(3), Cl(3)−Pd(1)−Cl(1) 91.96(3), Cl(2)−Pd(1)−Cl(1) 84.73(3), P(1)−Pd(1)−Pd(2) 124.21(2), Cl(3)−Pd(1)−Pd(2) 130.51(3), Cl(2)−Pd(1)−Pd(2) 50.41(2), Cl(1)−Pd(1)−Pd(2) 52.03(2), P(2)−Pd(2)−Cl(4) 92.14(3), P(2)−Pd(2)−Cl(2) 93.32(3), Cl(4)−Pd(2)−Cl(2) 173.05(3), P(2)−Pd(2)−Cl(1) 169.56(3), Cl(4)−Pd(2)−Cl(1) 91.01(3), Cl(2)−Pd(2)−Cl(1) 84.37(3), P(2)−Pd(2)−Pd(1) 133.18(2), Cl(4)−Pd(2)−Pd(1) 122.54(2), Cl(2)−Pd(2)−Pd(1) 50.537(19), Cl(1)−Pd(2)−Pd(1) 51.41(2).

Table 1. Crystal Data and Structure Refinement Details for Compounds **2**, **2′**, and **4**

	2	**2′**	**4**
empirical formula	$C_{40}H_{38}Cl_{10}P_2Pd_2$	$C_{40}H_{38}Cl_{10}P_2Pd_2$	$C_{40}H_{52}Cl_2O_{3.50}P_2Rh$
fw	1147.94	1147.94	927.48
temp (K)	173(1)	173(1)	295(1)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syst	orthorhombic	orthorhombic	triclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
a (Å)	11.304(1)	11.310(8)	12.961(8)
b (Å)	15.752(2)	15.757(1)	13.725(8)
c (Å)	24.733(3)	24.744(2)	15.125 (9)
α (deg)	90°	90°	83.6920(10)°
β (deg)	90°	90°	66.6190(10)°
γ (deg)	90°	90°	62.3430(10)°
V (A^3)	4403.8(9)	4409.8(6)	2178.4(2)
Z	4	4	2
calcd density (mg/m^3)	1.731	1.729	1.414
abs coeff (mm^{-1})	1.526	1.524	0.988
F(000)	2280	2280	948
cryst size (mm)	0.27 × 0.13 × 0.11	0.28 × 0.14 × 0.10	0.20 × 0.13 × 0.10
θ range, data collection (deg)	1.65 to 25.00°	1.65 to 25.00°	1.89 to 27.00°
limiting indices	$-13 \le h \le 13$ $-18 \le k \le 18$ $-29 \le l \le 29$	$-13 \le h \le 13$ $-18 \le k \le 18$ $-29 \le l \le 29$	$-16 \le h \le 16$ $-17 \le k \le 17$ $-19 \le l \le 19$
no. of reflns collected	43215	43627	25119
no. of indep reflns	7755	7762	9452
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	7755/0/491	7762/0/491	9452/0/477
goodness of fit on F^2	0.977	0.977	0.933
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0221, wR2 = 0.0475	R1 = 0.0281, wR2 = 0.0519	R1 = 0.0375, wR2 = 0.0939
R indices (all data)	R1 = 0.0239, wR2 = 0.0479	R1 = 0.0307, wR2 = 0.0526	R1 = 0.0548, wR2 = 0.0975
absolute structure parameter	−0.033(16)	−0.04(2)	−
Largest diff. peak and hole	0.490 and −0.306 e $Å^{-3}$	0.634 and −0.319 e $Å^{-3}$	0.631 and −0.272 e $Å^{-3}$

compared to that found in the monometallic *trans*-$PdCl_2$(L2)[17a] (5.766 Å versus 4.502 Å). On the other hand, the stronger bending of the Pd_2Cl_4 unit in **2** relative to that in **1** results in some reduction of this value (5.766 Å versus 5.907 Å). The terminal chlorine atoms, as expected, adapt a syn conformation with Pd(1)−Cl(3) and Pd(2)−Cl(4) distances of 2.282(8) and 2.284(8) Å, respectively. This and other structural parameters are within the normal range.

Intriguingly, we found that chiral but racemic **2** crystallizes in the acentrosymmetric space group $P2_12_12_1$ (Table 1).[19] If so, its crystals should consist of one of two enantiomorphs. Therefore, other crystals were analyzed as well. Flack parameters calculated for enantiomeric crystal structures were −0.033 and −0.04, illustrating that the separation of the two enantiomers spontaneously occurred during the crystallization.[19c]

Figure 5 represents the ORTEP drawings for (9*R*,10*S*) isomer of **2**.

The synthesis of bimetallic complexes of other metals was sought as well. For example, we found that bimetallic $[Rh_2Cl_2(CO)_2L1]$ (**4**) can be efficiently prepared using the ring-expansion reaction. The existence of bent $Rh_2(\mu\text{-}Cl)_2X_4$ complexes is not surprising: as was shown theoretically, rhodium halide dimers are mostly bent because of the relative diffuse nature of their atomic orbitals, in particular, if bearing strong *σ*-donor ligands.[20] Moreover, some quasi-closed chloride-bridged compounds of the described type have been structurally characterized.[13] However, to the best of our knowledge, all of these compounds were prepared kinetically starting from the corresponding rhodium dimer.[13,21] Therefore, it was fascinating to attempt this synthesis using the ring-expansion reaction.

To this end, we prepared and fully characterized the monometallic RhCl(CO)L1 (**3**)[22] compound to be used as a

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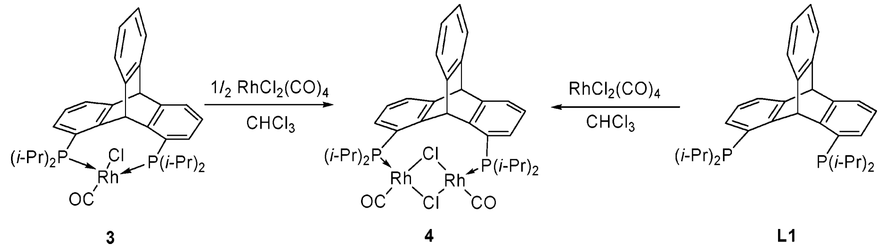
(19) (a) Jacques, J. J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Wiley: New York, 1981. (b) Collet, A.; Brienne, M.-J.; Jacques, J. *Chem. Rev.* **1980**, *80*, 215. (c) To exclude the possibility of an incorrect determination of the absolute configuration of **2**, the structure was inverted and the Flack parameter was recalculated. A Flack parameter of 1.0263 was found for the intentionally inverted (wrong) configuration of **2**.

(20) (a) Schnabel, R. C.; Roddick, D. M. *Inorg. Chem.* **1993**, *32*, 1513. (b) Hofmann, P.; Meier, C.; Hiller, W.; Heckel, M.; Riede, J.; Schmidt, M. U. *J. Organomet. Chem.* **1995**, *490*, 51.

(21) The following manuscripts report about the isolation of the halide-bridged quasi-closed bimetallic species from the reaction mixtures, apparently, as a result of a ligand elimination process and, thus, may be seen as exceptions: (a) Thomas, C. M.; Mafua, R.; Therrien, B.; Rusanov, E.; Stoeckli-Evans, H.; Süss-Fink, G. *Chem.*−*Eur. J.* **2002**, *8*, 3343. (b) Thomas, C. M.; Süss-Fink, G. *Coord. Chem. Rev.* **2003**, *243*, 125.

(22) Synthesis of several rhodium complexes bearing triptycene-based ligands have been reported in the past: Ahlers, W.; Roeper, M.; Hofmann, P.; Warth, D. C. M.; Paciello, R. *PCT Int. Appl.* **2001**, WO 2001058589. However, no detailed structural information has been provided by the patent record.

Scheme 4. Synthesis of **4** by the Ring-Expansion Reaction from **3** or from L1 and the Corresponding Dimer



precursor to the bimetallic compound. The synthesis was accomplished through the mixing of 1 equiv of L1 with $^1/_2$ equiv of $Rh_2Cl_2(CO)_4$ in chloroform. ^{31}P{^{1}H} NMR measurements indicated that the complexation of rhodium with the ligand was complete within 45 min at room temperature. The ^{31}P{^{1}H} NMR spectrum of complex **3** displays a doublet with a resonance frequency of 39.16 ppm and a Rh−P coupling constant of 127 Hz. As was observed previously for monometallic palladium complexes, the signal ascribed to the central methine hydrogen atom appears in the ^{1}H NMR spectrum at a very low field (9.11 ppm), suggesting a close proximity of the hydrogen to the metal center. Unfortunately, we do not have the X-ray evidence for the trans-spanned geometry of the precursor **3**; however, the splitting of the phosphorus-coupled carbon signals into 1:2:1 triplets in the ^{13}C NMR spectra of **3** may be a good indication of this configuration. Numerous compounds forming AXX′ spin systems, where the two phosphorus nuclei couple with a large coupling constant (characteristic to the trans diphosphine complexes),[23] feature similar coupling.[24]

Complex **3** was then allowed to react with an additional $^1/_2$ equiv of $Rh_2Cl_2(CO)_4$, and the reaction was monitored by ^{31}P{^{1}H} NMR. The formation of a single new product was observed (Scheme 4). The new compound exhibited a signal that appeared as a deshielded doublet at 61.72 ppm ($J_{\mathrm{Rh-P}}$ = 171 Hz) in contrast to that observed for **3** (33.93 ppm). The conversion was quantitative after 12 h.

The compound possessing identical spectral characteristics can successfully be prepared starting from ligand L1 and 1 equiv of the rhodium dimer $Rh_2Cl_2(CO)_4$.

Suitable single crystals of **4**, grown by the slow diffusion of pentane into their saturated solutions in THF at room temperature, were subjected to X-ray diffraction analysis (see Table 1 for crystallographic parameters). As we expected, the resulting **4** showed the bent arrangement of the Rh_2Cl_2 core (Figure 6).

The Rh atoms in the dinuclear complex **4** are in slightly distorted square-planar configurations with the bond angles around the metals ranging between 84.76 and 93.11 Å (deviation from planarity is 0.05 Å). Terminal carbonyl ligands adapt a syn conformation with Rh(1)−C(33) and Rh(2)−C(34) distances of 1.806(8) and 1.799(8) Å, respectively (within the normal range). Rh(1)−Cl(1) and Rh(2)−Cl(1) (trans to phosphine) distances are only slightly longer than Rh(1)−Cl(2) and Rh(2)−Cl(2) distances (2.41 Å vs 2.39 Å) and fall within the normal range. This difference can most likely be attributed to the slightly stronger trans influence of the phosphine over the carbonyl ligand.

The deformation of the Rh_2Cl_2 rhombus is very strong: the interplanar angle between the Rh(1)−Cl(1)−Cl(2) and Rh(1)−Cl(1)−Cl(2) planes is 114.58°, while the Rh−Rh separation is normal compared to the previously published *syn*- and *anti*-$Rh_2(\mu\text{-}Cl_2)(CO)_2$ quasi-closed complexes.[13]

Complex **4** was found to be air- and moisture-stable and perfectly soluble in common organic solvents (CH_2Cl_2, toluene, THF, DMSO, etc.) without notable decomposition. The complex is very stable even when reacted with 2 equiv of pyridine for 3 h. However, the complete conversion into the parent **3** takes place if allowed to react with an excess of pyridine overnight. This behavior manifests a very stable nature of the bent dirhodium bridges.

These results are particularly interesting because of the

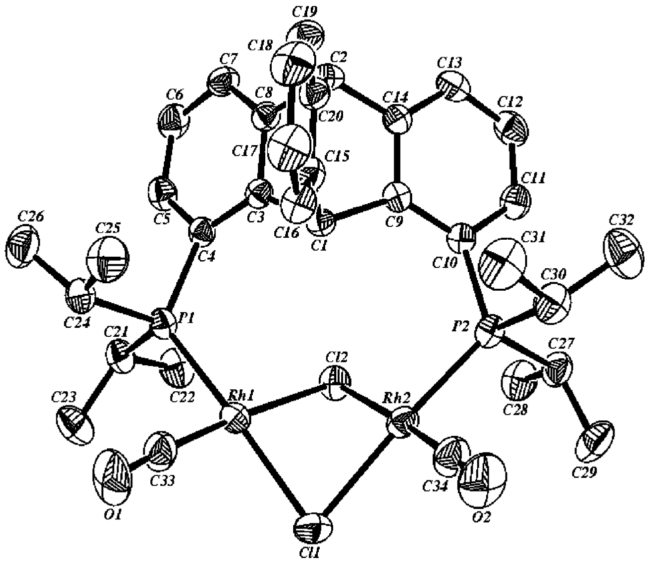


Figure 6. ORTEP drawing (50% probability ellipsoids) of the structure of **4**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cl(1)−Rh(1) 2.4085(10), Cl(1)−Rh(2) 2.4119(11), Cl(2)−Rh(1) 2.3904(9), Cl(2)−Rh(2) 2.3919(9), P(1)−Rh(1) 2.2361(10), P(2)−Rh(2) 2.2309(10), C(33)−O(1) 1.141(4), C(33)−Rh(1) 1.799(4), C(34)−O(2) 1.138(5), C(34)−Rh(2) 1.806(4), C(4)−P(1) 1.843(3), C(10)−P(2) 1.839(3); Rh(1)−Cl(1)−Rh(2) 76.45(3), Rh(1)−Cl(2)−Rh(2) 77.18(3), C(33)−Rh(1)−P(1) 91.38(13), C(33)−Rh(1)−Cl(2) 175.50(13), P(1)−Rh(1)−Cl(2) 93.11(3), C(33)−Rh(1)−Cl(1) 90.69(13), P(1)−Rh(1)−Cl(1) 173.92(4), Cl(2)−Rh(1)−Cl(1) 84.87(3), C(34)−Rh(2)−P(2) 91.17(14), C(34)−Rh(2)−Cl(2) 176.05(13), P(2)−Rh(2)−Cl(2) 92.31(3), C(34)−Rh(2)−Cl(1) 92.00(14), P(2)−Rh(2)−Cl(1) 172.76(4), Cl(2)−Rh(2)−Cl(1) 84.76(4).

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[23] Redfield, D. A.; Cary, L. W.; Nelson, G. H. *Inorg. Chem.* **1975**, *14*, 50.

[24] (a) Fild, M.; Althoff, W. *J. Chem. Soc., Chem. Commun.* **1973**, 933. (b) Alexson, D. E.; Holloway, C. E. *J. Chem. Soc., Chem. Commun.* **1973**, 455.

recent observations of an unusual reactivity of dirhodium halide-bridged complexes in the methanol carbonylation reaction.[13c]

Conclusion

A series of bimetallic chloride-bridged complexes possessing a rare strongly bent $M_2(\mu\text{-}Cl_2)$ core have been prepared via the ring-expansion reaction and have been fully characterized. We demonstrated that steric properties of ligands can play a pivotal role in the synthesis of halide-bridged compounds with potentially "communicating" metal centers. The stability of the bridge was exceptionally high: no equilibrium between the mono- and bimetallic species was observed under high-dilution conditions. Moreover, we found that the complexes were stable even in the presence of limited quantities of added Lewis bases such as pyridine. These observations are important in the context of potential applications of the new bent quasi-closed bimetallic complexes in catalysis: one can expect the catalytic site to remain undissociated. On the other hand, the exceptional stability of the bimetallic complexes despite the conformational strain in the 10-membered ring implies stabilizing interactions between the metal centers. Finally, the spontaneous resolution of the dissymmetric **3** into enantiomerically pure antipodes was demonstrated. The latter will be used as seed crystals for the resolution of larger quantities of the racemic L2.

Further theoretical and experimental studies on the mechanism of the ring expansion (which is of interest by itself), the new bimetallic compounds,[25] their catalytic and physical properties, and the synthesis of heterobimetallic compounds are in progress.

Experimental Section

All manipulations were performed using the standard Schlenk technique under an atmosphere of dry N_2. Anhydrous solvents and metal precursors were purchased from Aldrich and used as delivered. Ligands L1 [1,8-bis(diisopropylphosphino)triptycene] and L2 (1-diisopropylphosphino-8-diphenylphosphino-triptycene) and complexes $PdCl_2(L1)$ and $PdCl_2(L2)$ were prepared using our published procedures.[17] NMR spectra were recorded on a Bruker instrument operating at 400 MHz for protons, 100 MHz for carbons, and 121 MHz for phosphorus. Diffraction data were collected with a Bruker APEX CCD instrument [Mo Kα radiation ($\lambda = 0.710\ 73$ Å)]. Crystals were mounted onto glass fibers using epoxy. Single-crystal reflection data were collected on a Bruker APEX CCD X-ray diffraction system controlled by a Pentium-based PC running the SMART software package.[26] The integration of data frames and refinement of the cell structure were done by the SAINT+ program package.[27] Refinement of the structure on F^2 was carried out by the SHELXTL software package.[28] Further information may be found within the CIF files provided as Supporting Information.

[Pd_2Cl_4(L1)] (1). A solution of $PdCl_2$(L1) (200 mg, 0.301 mmol) and $PdCl_2(CH_3CN)_2$ (78 mg, 0.301 mmol) in chloroform (6 mL) was stirred at 45 °C for 24 h. The yellow precipitate formed was filtered, washed with two portions (2−3 mL) of the same solvent, and redissolved in ca. 30−50 mL of chloroform. The analytically pure compound was obtained by the slow diffusion of pentane into a saturated chloroform solution (125 mg, 49%). ^1H NMR ($CDCl_3$): δ 8.08 (d, 1H, $J = 7$ Hz), 7.85 (s, 1H), 7.61 (d, 2H, $J = 5$ Hz), 7.46 (d, 1H, $J = 7$ Hz), 7.14−7.07 (m, 6H), 5.58 (s, 1H), 3.38−3.33 (m, 2H), 2.53−2.46 (m, 2H), 1.70 (dd, 6H, $J = 7$ Hz, $J = 11$ Hz), 1.38 (dd, 6H, $J = 7$ Hz, $J = 11$ Hz), 0.54 (dd, 6H, $J = 7$ Hz, $J = 13$ Hz), 0.44 (dd, 6H, $J = 7$ Hz, $J = 8$ Hz). ^{31}P NMR ($CDCl_3$): δ 56.49. Anal. Calcd for $C_{32}H_{40}Cl_4P_2Pd_2$: C, 45.69; H, 4.79. Found: C, 45.41; H, 4.95.

Synthesis of 1 under High-Dilution Conditions. A solution of $PdCl_2$(L1) in chloroform-*d* (0.5 mL, 7.5 mM) was mixed with a solution of $PdCl_2(CH_3CN)_2$ in the same solvent (0.5 mL, 7.5 mM). The progress of the reaction was followed by $^{31}P\{^1H\}$ NMR at 45 °C.

[Pd_2Cl_4(L2)] (2). A solution of $PdCl_2$(L2) (200 mg, 0.273 mmol) and $PdCl_2(CH_3CN)_2$ (70 mg, 0.273 mmol) in chloroform (6 mL) was stirred at 45 °C for 24 h. The yellow precipitate formed was filtered, washed with two portions (2−3 mL) of the same solvent, and redissolved in ca. 30−50 mL of chloroform. The analytically pure compound suitable for X-ray analysis was obtained by the slow evaporation of chloroform (125 mg, 73%). ^1H NMR ($CDCl_3$): δ 7.64−7.82 (m, 4H), 7.40−7.59 (m, 7H), 7.16−7.29 (m, 4H), 7.12 (t, 1H, $J = 7$ Hz), 6.94 (t, 1H, $J = 7$ Hz), 6.87 (t, 1H, $J = 7$ Hz), 6.55−6.73 (m, 2H), 6.31 (d, 1H, $J = 7$ Hz), 5.39 (s, 1H), 3.21−3.36 (m, 1H), 2.65−2.83 (m, 1H), 1.80 (dd, 3H, $J = 7$ Hz, $J = 11$ Hz), 1.53 (dd, 3H, $J = 7$ Hz, $J = 11$ Hz), 0.99 (dd, 3H, $J = 7$ Hz, $J = 13$ Hz), 0.77 (dd, 3H, $J = 7$ Hz, $J = 8$ Hz). ^{31}P NMR ($CDCl_3$): δ 56.53 (s), 32.74 (s). Anal. Calcd for $C_{38}H_{36}Cl_4P_2Pd_2$: C, 50.19; H, 3.99. Found: C, 50.32; H, 3.95.

[RhCl(CO)L1] (3). A solution of L1 (400 mg, 0.82 mmol) and $Rh_2Cl_2(CO)_4$ (159.6 mg, 0.41 mmol) in chloroform (8 mL) was stirred at room temperature for 24 h. The analytically pure compound was obtained by the slow diffusion of pentane into a saturated chloroform solution (446.1 mg, 83%). ^1H NMR (THF-d_8): δ 9.10 (s, 1H), 7.47 (d, 2H, $J = 8$ Hz), 7.41 (d, 1H, $J = 7$ Hz), 7.31 (d, 1H, $J = 7$ Hz), 7.01−7.13 (m, 5H), 6.96 (t, 1H, $J = 8$ Hz), 5.49 (s, 1H), 2.96−3.03 (m, 2H), 2.73−2.85 (m, 2H), 1.54 (dd, 6H, $J = 7$ Hz, $J = 11$ Hz), 1.44 (dd, 6H, $J = 7$ Hz, $J = 11$ Hz), 1.16 (dd, 6H, $J = 7$ Hz, $J = 13$ Hz), 1.10 (dd, 6H, $J = 7$ Hz, $J = 8$ Hz). ^{13}C ($CDCl_3$): δ 187.07 (dt, $J_{C-Rh} = 57$ Hz, $J_{C-P} = 15$ Hz), 152.03 (t, $J = 8$ Hz), 147.52, 147.36 (t, $J = 4$ Hz), 144.08, 129.13 (t, $J = 19$ Hz), 127.57, 125.83, 125.70, 125.37, 124.71, 123.77 (t, $J = 3$ Hz), 122.96, 55.23, 54.96 (t, $J = 6$ Hz), 24.21 (t, $J = 10$ Hz), 23.57 (t, $J = 10$ Hz), 20.99, 20.47 (t, $J = 3$ Hz), 18.25 (t, $J = 6$ Hz), 16.05. ^{31}P NMR (THF-d_8): δ 38.16 (d, $J_{P-Rh} = 127$ Hz). Anal. Calcd for $C_{33}H_{40}ClOP_2Rh$: C, 60.70; H, 6.17. Found: C, 60.57; H, 6.01.

[$Rh_2Cl_2(CO)_2$L1] (4). *Method A.* A solution of L1 (400 mg, 0.82 mmol) and $Rh_2Cl_2(CO)_4$ (319.2 mg, 0.82 mmol) in THF (8 mL) was stirred at room temperature for 24 h. Crystals suitable for X-ray

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(25) Attempts to prepare similar diplatinum complexes have been undertaken as well. Unfortunately, we cannot report about the isolation of a structurally characterized compound of this type by now, though we have a NMR indication that they form. For example, when 2 equiv of the *trans*-$PtCl_2(CH_3CN)_2$ were allowed to react with 1 equiv of L1, the formation of two products was observed by $^{31}P\{^1H\}$ NMR. The major signal was centered at 1.93 ppm flanked by ^{195}Pt satellites and had a $^1J_{Pt-P}$ coupling constant of 1848 Hz. This signal is undoubtedly ascribed to a monometallic $PdCl_2$(L1) complex. The appearance of the minor signal centered at a lower field of 38.11 ppm may be attributed to the desired bimetallic compound by analogy with previously described Pd and Rh complexes. Unfortunately, the isolation of this product did not work well so far, but experiments are in progress.

(26) *SMART-NT*, v. 5.6; Bruker AXS GMBH: Karlsruhe, Germany, 2002.

(27) *SAINT-NT*, v. 5.0; Bruker AXS GMBH: Karlsruhe, Germany, 2002.

(28) *SHELXTL-NT*, v. 6.1; Bruker AXS GMBH: Karlsruhe, Germany, 2002.

analysis were obtained by slow evaporation of the resulting clear solution (508.6 mg, 76%).

Method B. A solution of [RhCl(CO)L1] (200 mg, 0.306 mmol) and $Rh_2Cl_2(CO)_4$ (59.5 mg, 0.153 mmol) in chloroform (8 mL) was stirred at 45 °C for 24 h. The clear yellow solution resulted. The volatiles were evaporated in vacuo, providing the desired product as yellow powder (239.1 mg, 95%). ^{1}H NMR ($CDCl_3$): δ 8.59 (s, 1H), 7.99 (d, 1H, $J = 7$ Hz), 7.51 (d, 2H, $J = 7$ Hz), 7.39 (d, 1H, $J = 7$ Hz), 7.17 (t, 2H, $J = 7$ Hz), 6.98−7.12 (m, 4H), 5.44 (s, 1H), 2.03−2.17 (m, 2H), 2.53−2.46 (m, 2H), 1.57 (dd, 6H, $J = 6$ Hz, $J = 18$ Hz), 1.32 (dd, 6H, $J = 7$ Hz, $J = 17$ Hz), 0.49−0.46 (m, 12H). ^{13}C ($CDCl_3$): δ 185.93 (dd, $J_{C-Rh} = 82$ Hz, $J_{C-P} = 16$ Hz), 151.25 (d, $J = 11$ Hz), 147.74 (d, $J = 8$ Hz), 144.68, 143.99, 129.24, 126.62, 126.13 (d, $J = 2$ Hz), 124.99 (d, $J = 4$ Hz), 123.99 (d, $J = 6.26$ Hz), 123.58, 123.23, 123.10, 56.16, 51.38 (t, $J = 4$ Hz), 30.36 (d, $J = 33$ Hz), 24.75 (d, $J = 29$ Hz), 20.83 (d, $J = 7$ Hz), 19.83 (d, $J = 3$ Hz), 19.13 (d, $J = 2$ Hz), 16.39 (d, $J = 6$ Hz). ^{31}P NMR ($CDCl_3$): δ 61.71 (d, $J_{P-Rh} = 171$ Hz).

Reactions of the Bimetallic Complexes with Pyridine. The solution of **1** or **4** (0.01 mmol) in chloroform-*d* (3 mL) was treated with an appropriate amount of pyridine (1 M solution in chloroform-*d*), and the ^{31}P{^{1}H} NMR spectrum was recorded at the desired temperature.

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Supporting Information Available: X-ray crystallographic files in CIF format and copies of NMR spectra for all structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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