Transcyclometalation: A Novel Route to (Chiral) Bis-*Ortho*-Chelated Bisphosphinoaryl Ruthenium(II) Complexes

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The Ru^{II} complexes [RuCl(R−PCP)(PPh_3)] (R−PCP = $[C_6H_3\{CH(Me)PPh_2\}_2$-2,6$]^-$ (**7a**), $[C_6H_3\{CH(Et)PPh_2\}_2$-2,6$]^-$ (**7b**), or $[C_6H_2\{CH_2PPh_2\}_2$-2,6-$SiMe_3$-4$]^-$ (**9**)) were synthesized using distinct synthetic routes. One of these routes consists of the reaction of the parent arene compound R−PCHP (i.e., $C_6H_4\{CH(Me)PPh_2\}_2$-1,3 (**6a**), $C_6H_4\{CH(Et)PPh_2\}_2$-1,3 (**6b**), or $C_6H_3(CH_2PPh_2)_2$-2,6-$SiMe_3$-4 (**8**)) with [$RuCl_2(PPh_3)_3$] in 1,2-dichloroethane. Following this procedure, complexes **7a** and **7b** were obtained. However, desilylation of **8** was observed with concomitant formation of complex [RuCl($C_6H_3\{CH_2PPh_2\}_2$-2,6)(PPh_3)] (**4**). A second synthetic approach has been developed and applied in the high-yield synthesis of complexes **7a**, **7b**, and **9**. This method, a *transcyclometalation* (TCM) reaction, involves the interconversion of one cyclometalated ligand metal complex, M(C,E), into another complex M(C,E′) with the concomitant consumption and formation of the corresponding arenes HC,E′ and HC,E, respectively. Using this method, previously observed problems such as nontolerance to the presence of a $SiMe_3$ group, contamination of the final product by uncoordinated PPh_3, or the formation of paramagnetic impurities were overcome. Investigations in solution of the formation of these square-pyramidal Ru complexes using two-dimensional NMR techniques ($^1H-^1H$ COSY and $^{31}P-^1H$ COSY) have shown that both synthetic routes were stereoselective, yielding only three of the four expected stereoisomers of complexes **7a** and **7b**.

Introduction

During the last 10 years, the synthesis and reactivity of organometallic species containing monoanionic R−NCN,[1] R−PCP,[2−4] and R−SCS[5] terdentate (pincer) ligands (N = NR_2, P = PR_2, S = SR, C = aryl carbanion, and R = aryl or alkyl group; see Figure 1) have been the subject of increasing research. Complexes of such ligands have been used either as templates for the study of fundamental chemical processes (e.g., the mechanism of oxidative addition,[6] C−C,[1b,3,7] C−O,[8] and C−Si[9] bond cleavage/bond formation) or in the field of catalysis (e.g., ketone reduction by hydrogen transfer,[10] alkane dehy-

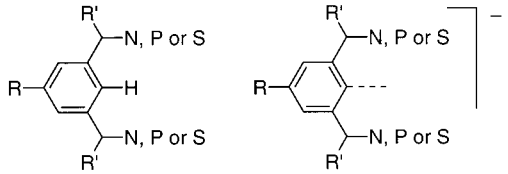

Figure 1. R−NCHN, R−PCHP, and R−SCHS type ligands and their corresponding anions.

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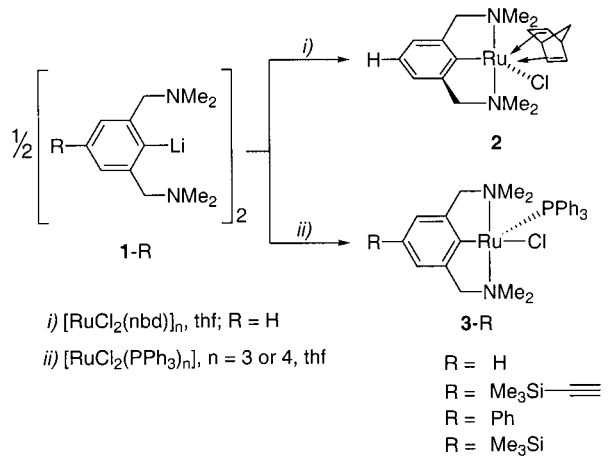
Scheme 1. Synthesis of [Ru(R−NCN)L$_n$] Complexes



drogenation,[11] Heck chemistry,[12] Kharasch addition,[13] and aldol condensation processes[14,15a]).

Recently, we reported on the synthesis of a variety of [RuCl(H−NCN)L$_n$] (N = NMe$_2$) complexes (e.g., **2** and **3**−R in Scheme 1) involving primarily a transmetalation reaction of dimeric organolithium species [Li(C$_6$H$_2${CH$_2$-NMe$_2$}$_2$-2,6-R-4)]$_2$ (**1**−R), with common Ru^{II} starting materials such as ([RuCl$_2$(PPh$_3$)$_n$] (n = 3 or 4) or [RuCl$_2$-(nbd)]$_n$, nbd = 1,5-norbornadiene).[16,17]

Despite the importance Ru compounds have as mediators and catalysts of organic transformations,[18] only a few examples of "pincer" Ru complexes containing PCP ligands are known. Moreover, the existing, well-defined, 16-electron [Ru^{II}X(R−PCP)L] complexes (in which R−PCP = [C$_6$H$_2$(CH$_2$PPh$_2$)$_2$-2,6-R-4]$^-$ and L = PPh$_3$; e.g., R = H (**4**)[4,19] and R = Ph (**5**)[4]) have been synthesized using [RuCl$_2$(PPh$_3$)$_3$] as starting material.[20] The synthesis of these compounds comprises a direct cyclometalation reaction of the *meta*-bisphosphinoarene ligand R−PCHP with [RuCl$_2$(PPh$_3$)$_n$] (n = 3 or 4) followed by net loss of one HCl. We have studied the scope of this process and encountered some drawbacks concerning the ruthenation of functionalized carbosilane dendrimers (i.e., R = SiMe$_3$, SiMe$_2$R$_{dendritic}$), since the released HCl was found to cleave the aryl C−Si bond even in the presence of base. To increase the tolerance of various R groups during the cyclometalation, we here report a new synthetic procedure,[21] a *transcyclometalation* (TCM) reaction. The TCM reaction involves the selective exchange of one bis-*ortho*-chelated ligand by another bis-*ortho*-chelated ligand and has hitherto not been recognized as such in the organometallic chemistry of tridentate monoanionic ligands.[22] An example is the 1:1 reaction of the *meta*-bisphosphinoarene ligand with a bisaminoaryl ruthenium(II) compound, affording the corresponding bisphosphinoarylruthenium(II) compound and the *meta*-bisaminoarene ligand.[22b] This TCM reaction sequence enables the direct synthesis of [RuX(H−PCP)L] complexes under mild conditions (no HCl release) and is illustrated here for the preparation of the (chiral) complexes **7** containing the monoanionic chiral ligand [C$_6$H$_3${CH(R′)PPh$_2$}$_2$-2,6]$^-$ (**7a**, R′ = Me; **7b**, R′= Et).

Results and Discussion

Ligand Synthesis. Ligands **6a**,**b** were synthesized on the basis of protocols developed by Zhang et al. (see Experimental Section for more details).[15] It should be noted that these chiral ligands were produced both via a nonstereoselective synthetic route giving a racemic mixture (i.e., a mixture of (*S*,*S*);(*R*,*R*)-enantiomers and the *meso*-diastereomer) and a stereoselective route (giving (*S*,*S*)-**6**). Residual minor impurities in the chiral ligand precursors due to racemization were removed by recrystallization from EtOAc, which left the *meso*-isomer in solution.

Synthesis of the Ruthenium Complexes via Direct Cyclometalation. The commonly applied route[4] for the synthesis of [Ru(PCP)]-type complexes comprises the reaction of a 1:1 molar mixture of the *meta*-bisphosphinoarene ligand with [RuCl$_2$(PPh$_3$)$_3$] in a chlorinated solvent (e.g., 1,2-dichloroethane) at reflux temperature.[23] Therefore, the synthesis of the chiral

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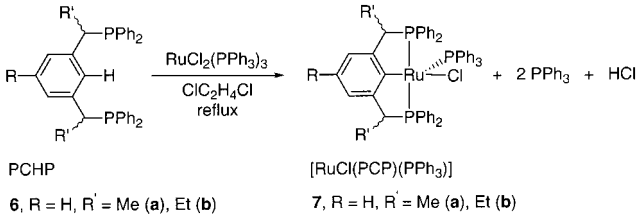
(23) The change of reaction solvent from CH$_2$Cl$_2$ (ref 3) to 1,2-dichloroethane resulted in a reduced reaction time and an increased yield. For instance, [RuCl$_2$(PPh$_3$)$_3$] and C$_6$H$_4$(CH$_2$PPh$_2$)$_2$-1,3 needed to be refluxed for 3 days in CH$_2$Cl$_2$ in order to give the respective complex **5** in 58% yield. In 1,2-dichloroethane, this period was reduced to 2 h with an isolated yield of 90%.

Scheme 2. Direct Cyclometalation of PCHP Affording 16-Electron Ruthenium(II)−PCP Complexes

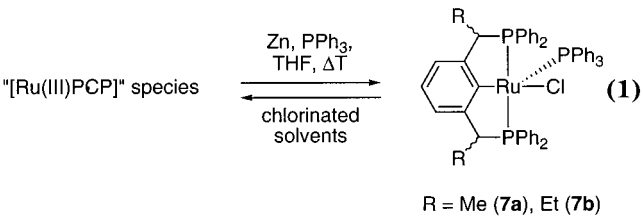


complexes **7a** and **7b** was first attempted using this methodology (see Scheme 2).

Reflux of an equimolar solution of **6a** and $[RuCl_2(PPh_3)_3]$ in 1,2-dichloroethane for 15 h afforded a green solution, from which, after workup, **7a** was obtained in 50% yield as a mixture of two diastereomers. Replacement of the methyl groups at benzylic positions for ethyl, i.e., the reaction of ligand **6b** with $[RuCl_2(PPh_3)_3]$ under the same conditions, had a pronounced effect on the rate of formation of the cycloruthenated product. The related green mixture of stereoisomers was obtained after 48 h of heating at reflux temperature. Unfortunately, **7b** could not be obtained free from uncoordinated PPh_3 due to similar solubility properties of these compounds in common organic solvents.

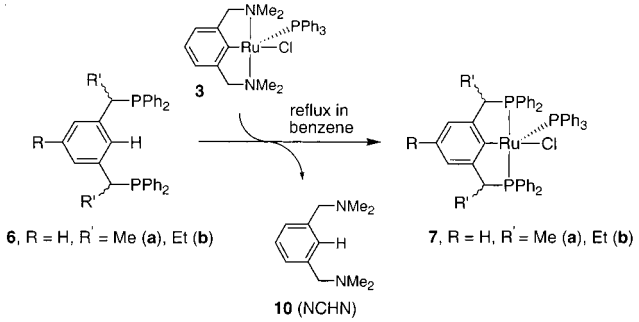
As complexes **7a** and **7b** were obtained as a mixture of stereoisomers, the NMR spectra were somewhat complicated but could be completely assigned (vide infra). However, it should be noted that besides the resonances related to the presence of **7a** and **7b**, the ^{31}P NMR spectra of a solution of the crude reaction mixtures in CD_2Cl_2 also showed two singlets: one at ca. −4.5 ppm, related to free PPh_3, and one at ca. 28 ppm, from an unknown compound. Indeed, addition of benzene or toluene to this solution caused selective precipitation of a red solid and concomitant disappearance of the resonance at 28 ppm. The ^1H NMR spectrum of this red material in CD_2Cl_2 at room temperature consisted of very broad resonances which remained unaffected by temperature variation in the range −100 to +25 °C, suggesting that the peak broadness is not caused by fluxional processes but more likely by the presence of paramagnetic Ru species (e.g., a Ru^{III} complex). The long reaction time and the use of a chlorinated solvent may be responsible for this oxidation (although a subsequent reaction with the liberated HCl cannot be ruled out). Accordingly, reflux of pure **7a** or **7b** in 1,2-dichloroethane led to slow formation of a similar red material (^{31}P NMR). Elemental analysis was not conclusive, but indicated the presence of phosphorus and chloride, the latter in a higher percentage as compared with **7a** or **7b**, respectively.

Reductive treatment of the red solid, isolated from the reaction of **6b** with $[RuCl_2(PPh_3)_3]$, with an excess of zinc and PPh_3 in refluxing THF (eq 1) afforded again



(1)

Scheme 3. Transcyclometalation (TCM) Reaction as a Novel Method to Prepare Ru(PCP) Complexes (and NCHN) from Ru(NCN) and PCHP

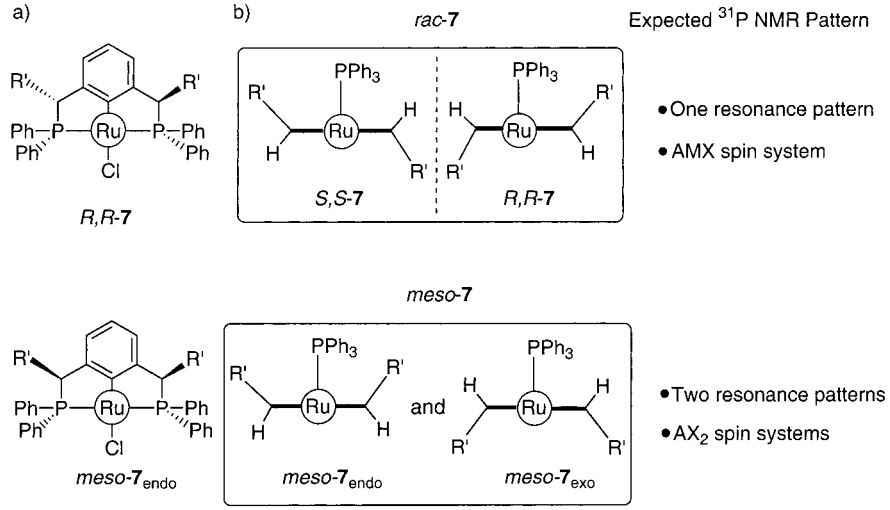


the mixture of stereoisomers of **7b** (^{31}P NMR). Consequently, the red solid is most likely comprised of ruthenium and PCP ligand in a similar ratio as in **7b**.

Synthesis of [RuCl(R−PCP)(PPh_3)] Complexes via Transcyclometalation (TCM). We observed that the NCN anion in $[RuCl(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)(PPh_3)]$ (**3**) can be substituted quantitatively by the PCP anion in a 1:1 molar reaction of **3** with the *meta*-bisphosphinoarene $C_6H_4(CH_2PPh_2)_2$-1,3 (**11**).[21] Therefore, this reaction was also applied to PCHP-type ligands **6a** and **6b** (Scheme 3). Reaction of the ligands **6a** or **6b** with **3** in a 1:1 molar ratio in refluxing benzene afforded the corresponding complexes **7a** and **7b**, respectively, in nearly quantitative yield (as established by NMR) with NCHN as the only other product. Isolation of the complexes was achieved by precipitation with cold hexane from a reaction solution in CH_2Cl_2 in 70 and 40% yield, respectively.

Structural Aspects of 7a and 7b in Solution. Due to the square-pyramidal geometry around ruthenium in the complexes described here, up to four stereoisomers of **7a** (or **7b**) are expected upon reaction of racemic **6a** (or **6b**) with **3**: the (*S*,*S*)-**7**;(*R*,*R*)-**7** enantiomeric pair (*rac*-**7**) and the two unique diastereomers (*S*,*R*)-R'_{endo} (*meso*-$\mathbf{7}_{endo}$) and (*R*,*S*)-R'_{exo} (*meso*-$\mathbf{7}_{exo}$). Chart 1 shows their stereochemistry and the expected ^{31}P NMR patterns. In the *meso*-$\mathbf{7}_{endo}$ stereoisomer, both R′ groups, i.e., the benzylic substituents methyl or ethyl, and the apical PPh_3 are on the same side of the Ru−C_{ipso}−Cl−P_2 plane (Chart 1), whereas in the *meso*-$\mathbf{7}_{exo}$ isomer, the R′ groups and the PPh_3 ligand are on opposite sides of this plane. For the interpretation of the NMR spectra, it is important to note that *meso*-$\mathbf{7}_{endo}$ and *meso*-$\mathbf{7}_{exo}$ are diastereomers, i.e., have different NMR spectroscopic properties. Note that by exchange of the PPh_3 ligand between apical positions via Ru−P bond dissociation/association, these two diastereomers are interconverted. In the case of the pair of enantiomers, one of the R′ groups is exo to the apical ligand while the other R′ group is orientated in an endo fashion. These isomers have the same spectroscopic properties, i.e., give rise to identical NMR resonance patterns. In conclusion, when all four isomers (*meso*-$\mathbf{7}_{endo}$, *meso*-$\mathbf{7}_{exo}$, and *rac*-**7**) are present in solution, in principle three different NMR patterns are expected. Spectroscopic analysis pointed out that **7a** and **7b** have similar structural features in solution as was already established for $[RuCl(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)(PPh_3)]$ (**3**)[16] and $[RuCl(C_6H_3\{CH_2PPh_2\}_2\text{-}2,6)(PPh_3)]$ (**4**),[4,19a,24] i.e., a distorted square-pyramidal

Chart 1. Newman Projections of the [RuCl(PCP)(PPh_3)] Complexes of the Ligands 6a,b[a]



[a]View of the benzylic substituents (a) along the P(PPh_3)-Ru axis (PPh_3—not shown—is in the front) and (b) along the C(4)–C_{ipso}–Ru–Cl axis (PPh_2 and chloride ligands in the front not shown).

Table 1. Selected ^1H and $^{31}P\{^1H\}$ NMR Data of Compounds 7a and 7b[a,b]

	δ ^1H (multiplicity)	δ ^{31}P (multiplicity, ^2J(PP) in Hz)	
compound	ArC–H	PCP	PPh_3
rac-**7a**	2.00–2.07 (m)	43.71 (dd, 20.7, 261.2)	80.10 (dd, 20.7, 46.8)
	4.29–4.36 (m)	58.37 (dd, 46.8, 261.7)	
meso-**7a**	2.80–3.00 (m)	54.54 (d, 32.4)	79.50 (t, 32.9)
rac-**7b**[c]	1.50–1.70 (m)	38.04 (dd, 19.8, 254.4)	79.81 (dd, 19.8, 48.0)
	4.05–4.15 (m)	55.06 (dd, 48.0, 254.4)	
meso-**7b**[c]	2.41–2.50 (m)	55.03 (d, 32.4)	77.73 (t, 32.4)

[a] Spectra recorded at 25 °C in benzene-d_6. ^1H chemical shifts (ppm) referenced to residual solvent signal. ^{31}P chemical shifts (ppm) referenced to external 85% H_3PO_4. [b]d, doublet; dd, double doublet; m, multiplet; t, triplet. [c]Spectra recorded at 25 °C in CD_2Cl_2.

geometry with the apical position occupied by the bulky PPh_3 ligand (see Scheme 2).

In earlier studies, we found that a "flip" of the fused puckered five-membered chelate rings in [RuCl(R–NCN)(PPh_3)], **3**–R, and [RuCl(R–PCP)(PPh_3)], **4** and **5**, is frozen on the NMR time scale (i.e., these compounds have mirror plane puckering) and all Ru–P bonds are persistent.[16,21] Thus, one can assume that the same is the case for the isomers of **7**; that is, each PPh_2 substituent has one equatorial and one axially orientated Ph group (Chart 1). Finally, Chart 1 also shows the view of representative isomers along the apical P–Ru axis. These projections show that whereas in the unique diastereomers *meso*-$\mathbf{7}_{endo}$ and *meso*-$\mathbf{7}_{exo}$ both halves of the PCP ligand are enantiotopic, in the enantiomeric pair these halves are diastereotopic. As a result, the $^{31}P\{^1H\}$ NMR spectrum related to *each meso*-$\mathbf{7}_{endo}$ and *meso*-$\mathbf{7}_{exo}$ diastereomer should be an AX_2 spin system (i.e., a doublet and a triplet) similar to the one observed in the ^{31}P NMR spectrum of the [RuCl(PCP)-(PPh_3)] compounds **4** and **9**. However, in the $^{31}P\{^1H\}$ NMR spectrum of the enantiomeric pair, an AMX spin system is expected. In view of the similarity of the spectroscopic data concerning these compounds, the focus will be centered on the spectroscopic features of **7b**.

The $^{31}P\{^1H\}$ NMR spectrum of **7b** shows one AMX spin system and only *one* AX_2 spin system, suggesting the formation of only one of the unique diastereomers (see Chart 1). It is important to note that this finding was not dependent on the synthetic route followed. The independence of these two patterns was unequivocally confirmed by a ^{31}P–^{31}P correlation NMR spectrum (^{31}P–^{31}P COSY). The PCP and PPh_3 phosphorus resonances of the diastereomer appear as a doublet at 55.03 and a triplet at 77.73 ppm, respectively (^2J(PP) = 32.4 Hz, Table 1). Like in the case of the achiral compounds, the observed spin system, coupling constants, and chemical shifts are consistent with a square-pyramidal structure containing one apical PPh_3 ligand in a *cis*-arrangement to two magnetically equivalent phosphorus atoms of the cyclometalated PCP ligand.[4,19,21]

All three phosphorus atoms of *rac*-**7b** have distinct chemical shifts and appear in the $^{31}P\{^1H\}$ NMR spectrum as doublets of doublets centered at 38.04, 55.06 (PCP phosphorus nuclei), and 79.81 ppm (PPh_3) (Figure 2). A characteristic *trans*-^2J(PP) of 254.4 Hz is observed for the *trans*-PCP phosphorus atoms, while the PPh_3 coupling constants with the PCP-phosphorus are much smaller and differ in magnitude (*cis*-^2J(PP) = 19.8 and 48.0 Hz).

In the ^{31}P–^1H COSY NMR spectrum of **7b** (Figure 2), the cross-peaks mark the positions of either P–Ph *ortho*-protons or benzylic protons related to the different stereoisomers. Therefore, the phosphorus nuclei from the unique diastereomer of *meso*-**7b** show four cross-peaks in total: one related to the PPh_3 at 6.90 ppm (thus, all PPh_3 *ortho*-protons are equivalent, implying free rotation about the Ru–PPh_3 bond on the NMR time scale) and three associated with the PCP phosphorus

(24) Dani, P.; van Klink, G. P. M.; van Koten, G. *Eur. J. Inorg. Chem* **2000**, 1465.

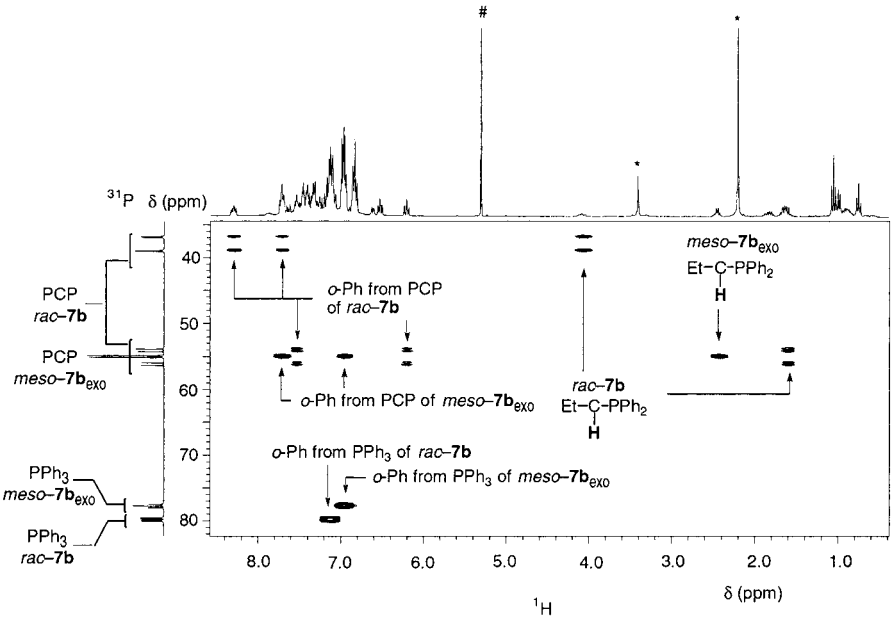


Figure 2. 121 MHz ^{1}H−^{31}P COSY of **7b** (*rac*/*meso* mixture) in CD_2Cl_2. Resonances labeled with (*) are from the free bisaminoarene ligand and with (#) from residual nondeuterated solvent.

atoms at 6.90, 7.70, and 2.45 ppm. This pattern of cross-peaks (already observed in similar analysis involving Ru complexes of nonchiral PCP ligands)[25] is a strong, independent piece of evidence that the Ru−C_{ipso}−Cl−P_2 plane is not a molecular symmetry plane, but the orthogonal plane involving the Cl−C_{ipso}−P(PPh$_3$) atoms is. Therefore, the *ortho*-protons of each diastereotopic phenyl group of the PPh$_2$ fragments are also diastereotopic and appear with a distinct chemical shift yielding the two cross-peaks at 6.90 and at 7.70 ppm. The only cross-peak at the nonaromatic region of the diastereomer *meso*-**7b** (at 2.45 ppm in the ^{1}H spectrum) reveals only one type of benzylic proton, which is either endo or exo orientated with respect to the apical phosphine ligand. This result together with the presence in the ^{13}C NMR spectrum of only one type of benzylic and methyl carbon for *meso*-**7b** is in accordance with the earlier conclusion that only one unique *meso* diastereomer is formed selectively.

As pointed out earlier, a common structural feature of [RuCl(R−PCP)(PPh$_3$)] complexes is the axial/equatorial positioning of the PPh$_2$ phenyl groups.[25a] Probably for purely steric reasons, one phenyl ring on each PPh$_2$ group occupies the vacant coordination site opposite the PPh$_3$ ligand. A consequence of this is a distinct puckering of the two fused five-membered rings which orientates one of the benzylic substituents (in the case of **7** most likely the smaller one, i.e., H) near the apical ligand; see Chart 1. This causes two interesting effects in the ^{1}H NMR spectra of these compounds that can be used as structural probes:[25a] (i) an upfield shift of the axial benzylic proton (most likely caused by shielding effects from the PPh$_3$ ligand), and (ii) the appearance of a cross-peak in the ^{1}H−^{1}H COSY NMR spectrum involving this axial benzylic proton and the xylylene protons H-3,5 in the PCP ligand.[26]

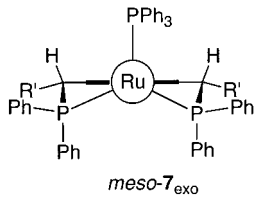


Figure 3. Newman projection of the obtained *meso*-**7**$_{exo}$ diastereomer. View along the C(4)−C_{ipso}−Ru−Cl axis. The chloride ligand (not shown) is in front (forward direction).

These spectroscopic features are observed in the NMR spectrum of the diastereomer and can be used to arrive at an assignment of its configuration. Thus, the chemical shift of the benzylic proton at 2.45 ppm is considerably upfield for a methine proton, and in the ^{1}H−^{1}H COSY NMR spectrum, a cross-peak is present involving this proton and the aryl protons H-3,5. Therefore, *meso*-**7b**$_{exo}$ and not *meso*-**7b**$_{endo}$ is present, and a more refined idea about the structure of this compound (in solution) is depicted in Figure 3. It is important to note that the presence of *meso*-**7**$_{endo}$ for both **7a** and **7b** has never been detected by ^{31}P NMR spectroscopy in the material obtained from both synthetic routes. The relative amount of *meso*-**7b**$_{exo}$ present after reaction, when compared with the amount of the *rac*-**7b** enantiomeric pair, implies that *meso*-**7b**$_{endo}$, if ever formed, is being converted into *meso*-**7b**$_{exo}$ and not, for instance, lost by decomposition processes.

The low molecular symmetry of the *rac*-**7b** is clearly indicated by the spectrum depicted in Figure 2. All phenyl rings of the PPh$_2$ groups are distinct, and for this reason four cross-peaks are present in the aromatic region related to the PCP phosphorus nuclei (two for

(25) (a) Dani, P.; Richter, B.; van Klink, G. P. M.; van Koten, G. *Eur. J. Inorg. Chem.*, in press. (b) del Río, I.; Gossage, R. A.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1999**, *583*, 69.

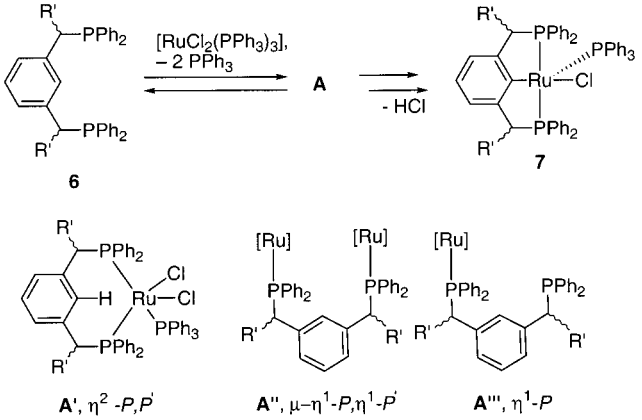
(26) The detection of the indirect coupling between benzylic and H-3,5 protons can be explained by analogy with allylic systems: the smaller the torsional angle between the benzyl C−H bond and the axis of the arene π-orbitals, the larger the four-bond coupling constant. See: (a) Friebolin, H., *Basic One- and Two-Dimensional NMR Spectroscopy*, 2nd ed.; VCH: Weinheim, 1993; p 83. (b) Günther, H. *NMR Spectroscopy−An Introduction*; John Wiley & Sons: New York, 1980; p 46.

each phosphorus resonance). The two cross-peaks in the nonaromatic region of the ^{1}H spectrum are consistent with the postulated structure and identify the resonances of the inequivalent benzylic protons related to each of the $-CH(Et)PPh_2$ substituents. Importantly, one of the benzylic protons (at 1.50−1.70 ppm) shows a behavior similar to that observed with the benzylic protons of *meso*-**7b**$_{exo}$. Thus, the signal of the benzylic proton at 1.62 ppm is considerably upfield for a methine proton and shows also a cross-peak with H-3,5 in the ^{1}H−^{1}H COSY NMR spectrum. Therefore, this proton should be in an axial situation, pointing toward the apical position. Consequently, the other benzylic proton is expected to be equatorial. Indeed, it has a regular chemical shift (4.05−4.15 ppm) and does not show a cross-peak with H-3,5 in the ^{1}H−^{1}H COSY NMR spectrum. These assignments were unequivocally determined by spectroscopic analyses of the ruthenium complexes obtained by a TCM reaction of **3** with (*S*,*S*)-**6b** (vide infra). All signals in the NMR spectra assigned to the *meso*-complex were absent. Similarly, when (*S*,*S*)-**6a** was used as ligand precursor in a TCM reaction, the chiral complex (*S*,*S*)-**7a** was obtained in high yield. The ^{31}P NMR spectrum showed the expected AMX spin system only (Table 1), and two distinct signals for the benzylic protons were observed in the ^{1}H NMR spectrum. The methyl group appears as a multiplet around 1 ppm.

Formation of 7 via Direct Cyclometalation. Although the result of both processes depicted in Scheme 2 and Scheme 3 is formally the substitution of an aromatic proton by the cationic metal fragment [RuCl(PPh$_3$)], the reaction profiles differ significantly. ^{31}P NMR analysis after 1 h of the reaction mixture obtained by reacting **6a** via direct cyclometalation showed the presence of two distinct groups of AX_2 and AMX spin systems. One group was sharp and clearly results from the formation of some of the *rac*-**7a** and *meso*-**7a**$_{exo}$ stereoisomers. The other was broader and located at much higher field (the AM part of the spin system was spread between −5 and 20 ppm, while the X part was observed between 40 and 42 ppm). During the course of the reaction the latter group of signals disappeared with concomitant increase of the intensity of the resonances related to the final products (including a broad singlet related to the paramagnetic material mentioned above). The spin systems observed at higher field indicate that the intermediates formed have three phosphorus atoms per Ru center, and the chemical shifts strongly suggest that the R−PCHP ligand has not undergone a cyclometalation. An η^2-*P*,*P*′-coordinated R−PCHP ligand (e.g., **A**′ in Scheme 4) is a likely structure to explain these facts. Other potential intermediates include bridging R−PCHP ligands forming open chain structures. However, this hypothesis is weakened by the fact that ruthenium(II) compounds containing (achiral) R−PCHP ligands in a μ-η^1-*P*, η^1-*P*′, or η^1-*P* bonding mode (i.e., species such as **A**″ and **A**‴, respectively, with R′ = H) have been observed and all have ^{31}P chemical shifts at lower field than 40 ppm.[25]

Species containing an η^2-*P*,*P*′-R−PCHP ligand have been proposed as intermediates for the selective metalation of the *ipso*-carbon of R−PCP systems.[2c,4,8,21,27] Vacant sites that are necessary for C−H activation to occur are probably accomplished by phosphine decoordination, either of a PCHP or PPh$_3$. In the case of an η^2-*P*,*P*′→η^1-*P* rearrangement of the PCHP ligand, open chain structures are formed (e.g., **A**″ and **A**‴, Scheme 4).[25]

Scheme 4. Possible Intermediates Obtained during the Formation of [RuCl(R−PCP)(PPh$_3$)] Complexes via Direct Metalation



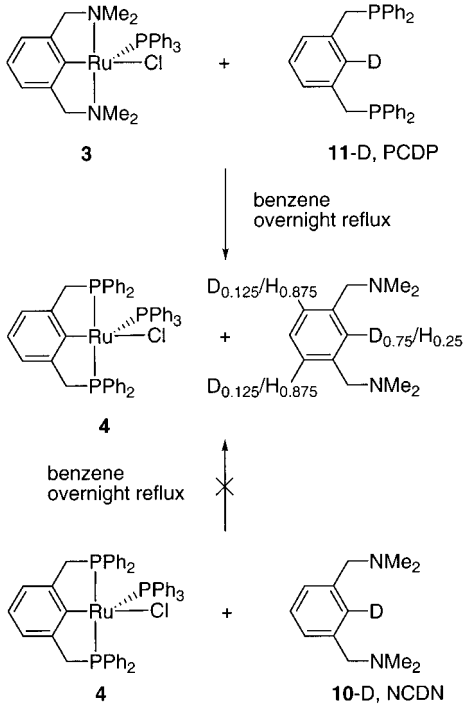
Formation of 7 via TCM. The reaction between **6b** and **3** (see Scheme 3) in benzene-d_6 was followed by ^{31}P NMR spectroscopy. No reaction was observed at room temperature. The first signals of the final products became visible only after 30 min at 60 °C. Besides the resonances related to the starting materials and final products, and a broad signal at −5 ppm indicating the presence of free PPh$_3$, no other species were observed. Preliminary kinetic measurements at 60 °C showed this reaction to be first-order in PCHP and in **3** but zero-order in product formation. These results indicate that the products are not directly formed from the reactants, but through undetected intermediate species. Moreover, the (pseudo) zero-order rate law deduced for product formation indicates complicated reaction kinetics and is not conclusive whether the final transformations occur inter- or intramolecularly.[28] It is difficult to speculate on the structures of potential intermediate(s) with the limited data available.

To get more insight into the mechanism of the TCM reaction, **3** was reacted with the deuterated ligand $C_6H_3(CH_2PPh_2)_2$-1,3-D-2 (**11**-D (PCDP) in nondeuterated benzene (Scheme 5). ^{1}H and ^{2}H NMR analysis of the resulting Ru complex **4** did not reveal incorporation of deuterium at any specific position in its structure. However, similar analysis of the resulting *meta*-bisaminoarene ligand showed a deuterium presence mainly at the former *ipso*-carbon (i.e., at C-2) and a lower percentage (total ca. 25%) at the nonmutual *ortho*-positions (C-4,6). In this case, it was not possible to confirm whether monodeuterated or polydeuterated species were formed. Most importantly, when [RuCl(PCP)(PPh$_3$)], **4**, and $C_6H_3(CH_2NMe_2)_2$-1,3-D-2 (**10**-D (NCDN) were refluxed overnight in benzene, deuterium loss or inter-

(27) See for instance: (a) Bennett, M. A.; Johnson, R. N.; Tomkins, I. B. *J. Organomet. Chem.* **1977**, *128*, 73. (b) Lesueur, W.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1997**, *36*, 3354. (c) Baltensperger, U.; Guenter, J. R.; Kägi, S.; Kahr, G.; Marty, W. *Organometallics* **1983**, *2*, 571

(28) For example, in TCM reactions of [PtCl(H−NCN)] with H−PCHP we were able to isolate a complex containing a μ-η^1-*P*, η^1-*P*′ H−PCHP ligand with a (Pt−)Cl···H(−C) bond that is responsible for the cyclometalation process. See ref 22b.

Scheme 5. Mapping of the Deuterium Transfer in the Transcyclometalation Reaction (See Scheme 2)

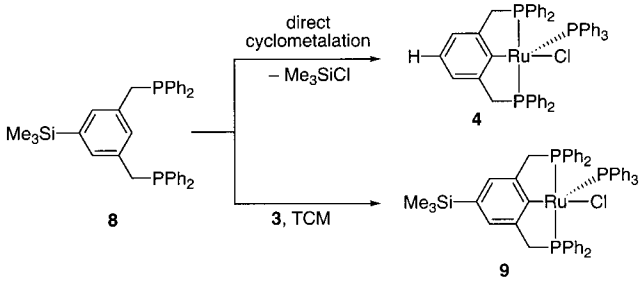


molecular deuterium scrambling was not detected, indicating that complex **4** alone is not able to promote the processes described previously.

The preferential transfer of a deuterium atom from PCDP to the metalated *ipso*-carbon of the bisaminoaryl NCN ligand can be understood on the basis of an initial overall oxidative addition of the C−D bond of the PCDP ligand to the ruthenium center, forming Ru-D intermediates[29] that reductively eliminate NCDN. However, the amino groups of the NCN ligand may play an important role in the process of deuterium transfer as well as in the mechanism that leads to the deuterium reallocation from C-2 to the C-4,6 carbons of the *meta*-bisaminoaryl ligand.[28] Therefore, Ru-D species are not necessarily involved. However, no clear evidence for such ligand assistance could be observed, and further investigations are currently underway.

Application of Transcyclometalation Reaction. The synthesis of the ligand $C_6H_3(CH_2PPh_2)_2$-3,5-Me_3-Si-1 (**8**) can be seen as a model route for the grafting of a PCHP ligand to a carbosilane dendrimer. A similar approach has already been followed for the attachment of NCHN ligands[30a,b] to the periphery of polymers and dendrimers, which in turn can be used for the synthesis of multisite catalysts.[30,31] Ligand **8** was obtained in high yield (93%) by treating $C_6H_3(CH_2PPh_2)_2$-3,5-Br-1 with 2 equiv of *t*-BuLi at −78 °C followed by a quench of the reaction mixture with Me_3SiCl.

Scheme 6. Cleavage of the Si−C Bond during Ruthenation of 8 under Direct Cyclometalation Conditions



Reaction of **8** under the conditions of direct cyclometalation led to the formation of known [RuCl-($C_6H_3\{CH_2PPh_2\}_2$-2,6)(PPh_3)] (**4**) in 90% yield instead of the expected *para*-trimethylsilyl-substituted **9** (Scheme 6).[4,19] This was established by the identical spectroscopic characteristics of the isolated material and authentic **4** and also by the lack of any proton resonance upfield of 2 ppm, indicating the loss of a Me_3Si− group. Metathesis of the Me_3Si−C bond with the HCl formed during the ruthenation process is most likely the reason for the observed Si−C bond cleavage. Addition of base, for example, NEt_3, to the reaction mixture could only partially prevent the cleavage of the Si−C bond (60% yield of **9** based on NMR). This result indicated that the presence of a silane functionality in the PCHP ligand is not compatible with the conditions applied in the direct cyclometalation. Consequently, direct ruthenation of PCHP-terminated carbosilane dendrimers via direct cyclometalation is not a viable option, because this would lead to cleavage of the PCHP ligand from the dendritic periphery.

However, the mild conditions characteristic for the TCM reaction were suitable for the formation of **9**. Addition of **3** to **8** resulted in the formation of ruthenated PCP complex **9**. The ^{1}H NMR spectrum of **9** revealed a singlet at 0.33 ppm integrating for nine protons, confirming the presence of a Me_3Si− group. It also showed two characteristic multiplets at 2.45 (2H) and 3.50 ppm (2H) related to the diastereotopic benzylic protons. The ^{31}P NMR spectrum was typical for this class of complexes and consisted of a doublet at 36.98 ppm (PCP phosphorus nuclei) and a triplet at 82.73 ppm (PPh_3, ^2J(PP) = 32 Hz). The chemical shift[32] and coupling constant[33] are characteristic of an apical phosphine in a *cis* arrangement to two magnetically equivalent phosphorus atoms of a cyclometalated PCP ligand.[4,19,21]

The *meta*-bisaminoarene compound also formed during the reaction was isolated and characterized as H−NCHN (**10**) using NMR and mass spectrometric analysis. As chlorinated solvents are not used and HCl

(29) Formally, these species can be either formulated as Ru^{II}−H^+, with intramolecular base assistance of the N from H−NCN, or as Ru^{IV}−H^-. See refs 1c and 22b.

(30) (a) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659. (b) van Koten, G.; Jastrzebski, J. T. B. H. *J. Mol. Catal. A: Chem.* **1999**, *146*, 317. (c) Hovestad, N. J.; Hoare, J. L.; Jastrzebski, J. T. B. H.; Canty, A. J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1999**, *16*, 2970. (d) Kleij, A. W.; Kleijn, H.; Jastrzebski, J. T. B. H.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1999**, *18*, 268. (e) Kleij, A. W.; Kleijn, H.; Jastrzebski, J. T. B. H.; Spek, A. L.; van Koten, G. *Organometallics* **1999**, *18*, 277. (f) Kleij, A. W.; Jastrzebski, J. T. B. H.; van Koten, G. In *Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; John Wiley & Sons: Sussex, England, 2000, submitted.

(31) (a) van de Kuil, L. A.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Chem. Mater.* **1994**, *6*, 1675. (b) Pathmamanoharan, C.; Wijkens, P.; Grove, D. M.; Philipse, A. P. *Langmuir* **1996**, *12*, 4372.

(32) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221.

(33) (a) Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 797. (b) Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 141.

is not formally generated during a reaction via the transcyclometalation procedure, this reaction protocol suppresses undesired side reactions (cf. formation of a red compound or Si−C bond cleavage).

Conclusion

A new synthetic approach has been developed in which a *meta*-bisaminoaryl terdentate ligand NCN was quantitatively replaced by a corresponding *meta*-bisphosphinoaryl ligand R−PCP leading to the formation of [RuCl(R−PCP)(PPh_3)] complexes. Using this transcyclometalation (TCM) reaction, problems such as the presence of free phosphine or HCl or the need for the use of chlorinated solvents, which may give rise to secondary products, were overcome. The scope of this TCM reaction with other types of transition metal−NCN complexes is currently under investigation.

Experimental Section

General Comments. All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Benzene, toluene, alkanes, and THF were dried over sodium using benzophenone as indicator. Dichloromethane was dried over CaH_2. 1,2-Dichloroethane was degassed using the freeze−pump−thaw technique. ^1H, ^{13}C, and ^{31}P NMR were recorded at 25 °C on a Bruker AC200 or on a Varian Unity INOVA 300 NMR spectrometer. Chemical shifts are in ppm relative to residual solvent signal (^1H and ^{13}C NMR spectra) and a capillary containing 85% H_3PO_4 (^{31}P NMR spectra). $[RuCl_2(PPh_3)_3]$[34] and [RuCl($C_6H_3\{CH_2NMe_2\}_2$-2,6)(PPh_3)][16] (**3**) were prepared according to literature procedures. The ligand (*S,S*)-**6a** was prepared according to a modified literature procedure[15] and analogous to the synthesis of **6b** (see below). The alcohol $C_6H_4(CH(Et)OH)_2$-1,3 was obtained enantiopure or as a *rac/meso* mixture according to literature procedures.[35] All other reagents were purchased commercially.

Synthesis of (*S,S*)-$C_6H_4(CH(Et)PPh_2)_2$-1,3 ((*S,S*)-6b). A modified literature procedure was used.[15] To a THF (60 mL) solution of $C_6H_4(CH(OH)Et)_2$-1,3 (3.76 g, 19.4 mmol) was added a solution of *n*-BuLi (30 mL, 45 mmol; 1.5 M in hexane) at room temperature. The resulting purple suspension was cooled to −80 °C, and $MeSO_2Cl$ (3.5 mL, 45 mmol) was added dropwise during 20 min. After 2 h stirring, a THF solution of $LiP(BH_3)Ph_2$ (prepared from *n*-BuLi (28 mL, 42 mmol) and $HP(BH_3)Ph_2$ (8.40 g, 42 mmol) in THF (30 mL)) was added and the mixture stirred at −80 °C for 2 h. After slow warming to room temperature and prolonged stirring (12 h), water was added (80 mL) and the layers were separated. The aqueous phase was extracted with Et_2O (2 × 60 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and filtered, and all volatiles were removed in vacuo. The residual mixture was further purified by column chromatography (SiO_2, hexane/CH_2Cl_2, 3:1), yielding a white solid (4.10 g, 41%). Recrystallization from EtOAc yielded analytically pure (*S,S*)-**6b**·$2BH_3$. Anal. Calcd (Found): C 77.45 (77.46), H 7.58 (7.66), P 11.10 (11.05). Mp: 166−169 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.67 (t, ^3J(HH) = 6.9 Hz, 6H, CH_3), 1.86−2.09 (m, 4H, CH_2), 3.38 (ddd, ^3J(HH) = 11.7 Hz, ^3J(HH) = 3.3 Hz, ^2J(HP) = 16 Hz, 2H, CH−P), 6.92−7.08 (m, 4H, aromatic), 7.14−7.36 (m, 9H, aromatic), 7.46−7.56 (m, 7H, aromatic), 7.84−7.94 (m, 4H, aromatic). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 12.93 (d, ^3J(CP) = 13.4 Hz, CH_3), 23.86 (d, ^2J(CP) = 4.9 Hz, CH_2), 45.21 (d, ^1J(CP) = 30.9 Hz, CH−P), 127.6−133.1 (11 aromatic signals), 135.85 (s, aryl). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 24.75 (s).

Diagnostic signals for *meso*-**6b**·$2BH_3$: ^1H NMR (300 MHz, $CDCl_3$): δ 0.63 (t, ^3J(HH) = 7.2 Hz, 6H, CH_3), 1.72−1.92 (m, 4H, CH_2), 3.47 (ddd, ^3J(HH) = 11.4 Hz, ^3J(HH) = 3.3 Hz, ^2J(HP) = 16.5 Hz, 2H, CH−P). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 23.63 (d, ^2J(CP) = 4.9 Hz, CH_2), 44.94 (d, ^1J(CP) = 30.9 Hz, CH−P), 135.46 (s, aryl). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 23.97 (s).

The borane protecting group was quantitatively removed with HBF_4·OEt_2 following the procedure described in the literature.[15]

(*S,S*)-6b. ^1H NMR (300 MHz, $CDCl_3$): δ 0.69 (t, ^3J(HH) = 7.2 Hz, 6H, CH_3), 1.60−1.85 (m, 4H, CH_2), 3.15−3.35 (m, 2H, CH−P), 6.80−7.20 (m, 14H, aromatic), 7.35−7.50 (m, 6H, aromatic), 7.60−7.75 (m, 4H, aromatic). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 12.52 (d, ^3J(CP) = 11.2 Hz, CH_3), 26.69 (d, ^2J(CP) = 21.2 Hz, CH_2), 47.23 (d, ^1J(CP) = 11.8 Hz, CH−P), 126.71, 127.25, 127.66 (all m, aryl), 127.85, 128.01, 128.07, 128.18 (all s, aryl), 128.45 (m, aryl), 129.01 (s, aryl), 129.75 (m, aryl), 130.92 (m, aryl), 133.11 (d, J(CP) = 18.1 Hz, aryl), 133.25 (d, J(CP) = 20.3 Hz, aryl), 137.00−137.60 (m, aryl), 140.60−140.95 (m, aryl). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ −0.61 (s).

Diagnostic signals for *meso*-**6b**: ^1H NMR (300 MHz, $CDCl_3$): δ 0.71 (t, ^3J(HH) = 7.2 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 12.63 (d, ^3J(CP) = 11.8 Hz, CH_3), 26.50 (d, ^2J(CP) = 21.8 Hz, CH_2). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ −0.48 (s).

Synthesis of [RuCl($C_6H_3\{CH(Me)PPh_2\}_2$-2,6)(PPh_3)] (7a). Direct Cyclometalation. Complexes **7a** were synthesized using ligand **6a** following the same procedure described in route 1 for complex **7b** (see below). After overnight heating at reflux temperature, the solution was concentrated and layered with pentane, causing a coprecipitation of a red and a green material. These species were washed with pentane until analysis by ^{31}P NMR spectroscopy indicated that free PPh_3 was no longer present. A subsequent extraction with benzene followed by filtration separated **7a** from the red solid (the latter is insoluble in benzene). Yield: 50%. MS (FAB^+): *m/z* 900.3 ($M^{\bullet+}$, $C_{52}H_{46}{}^{35}ClP_3{}^{102}Ru$), 865.4 ([M − Cl]$^+$), 638.1 ([M − PPh_3]$^+$), 603.1 ([M − PPh_3 − Cl]$^+$).

Transcyclometalation. The same procedure described in route 2 for complex **7b** (see below) was used here, and complex **7a** was obtained in 68% yield after overnight heating at reflux temperature.

Note: During the synthesis of ligand **6a**, the *meso* isomer was partially lost by crystallization (only 22% of the *meso* form was present). Consequently, not all spectroscopic features of the *meso*-**7a** could be observed, particularly some ^{13}C resonances.

(*S,S*)-7a. ^1H NMR (300 MHz, C_6D_6): δ 0.84 (dd, ^3J(HH) = 7.5 Hz, ^3J(HP) = 14.7 Hz, 3H, CH_3), 0.96 (dd, ^3J(HH) = 6.6 Hz, ^3J(HP) = 12.0 Hz, 3H, CH_3), 2.00−2.07 (m, 1H, CH-Me), 4.29−4.36 (m, 1H, C*H*-Me), 6.20−8.60 (aromatic protons). $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2): δ 15.09 (d, ^2J(CP) = 15.1 Hz, CH_3), 17.15 (d, ^2J(CP) = 2.8 Hz, CH_3), 39.61 (d, ^1J(CP) = 30.4 Hz, CH), 45.09 (d, ^1J(CP) = 29.0 Hz, CH), 121.94 (d, J(CP) = 16.6 Hz), 122.89 (s,), 123.55 (d, J(CP) = 15.7 Hz), 126.40−130.40 (m), 132.09 (s), 133.20−136.00 (m), 136.97 (d, ^1J(CP) = 50.7 Hz, C_{quat}−PPh_3), 155.20 (d, J(CP) = 15.2 Hz, C_{quat}−CH_2−PPh_2), 157.94 (d, J(CP) = 18.3 Hz, C_{quat}−CH_2−PPh_2), 171.56 (d, ^1J(CP) = 15.2 Hz, Ru-C_{ipso}). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 43.71 (dd, ^2J(PP) = 20.7 Hz, ^2J(PP) = 261.2 Hz, 1P, PPh_2), 58.37 (dd, ^2J(PP) = 46.8 Hz, ^2J(PP) = 261.7 Hz, 1P, PPh_2), 80.10 (dd, ^2J(PP) = 20.7 Hz, ^2J(PP) = 46.8 Hz, PPh_3).

(*meso*)-7a. ^1H NMR (300 MHz, C_6D_6): δ 1.30−1.40 (m, residual signal of the CH_3), 2.80−3.00 (m, residual signal of the C*H*-Me), 6.20−8.60 (aromatic protons). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 54.54 (d, ^2J(PP) = 32.4 Hz, 2P, PPh_2), 79.50 (t, ^2J(PP) = 32.9 Hz, 1P, PPh_3).

Synthesis of [RuCl($C_6H_3\{CH(Et)PPh_2\}_2$-2,6)(PPh_3)] (7b). Direct Cyclometalation. A mixture (1.0 g, 1.9 mmol) con-

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taining the *R,R;S,S* and *R,S/S,R* isomers of the bisphosphine $C_6H_4(CH(Et)PPh_2)_2$-2,6 (**6b**) was dissolved in 1,2-dichloroethane and then added to a boiling slurry of $[RuCl_2(PPh_3)_3]$ (1.8 g, 1.9 mmol) in the same solvent. After 48 h of heating at reflux, a green solution was formed containing free PPh_3, an unidentified compound, and a 1:1 mixture of the diastereomers of **7b**. Attempts to obtain pure **7b** by precipitation from the 1,2-dichloroethane using hexane were not successful due to the similar solubility of **7b** and free PPh_3.

Transcyclometalation. A mixture (40 mg, 76 μmol) containing the *R,R;S,S* and *R,S/S,R* isomers of the bisphosphine $C_6H_4(CH(Et)PPh_2)_2$-2,6 (**6b**) was dissolved in benzene (2 mL) and transferred to a Schlenk flask containing $[RuCl(C_6H_3\{CH_2NMe_2\text{-}2,6\})(PPh_3)]$ (45 mg, 76 μmol) in 2 mL of benzene at room temperature. After 48 h of heating at reflux, the reaction mixture was concentrated in vacuo until only a small residual amount of liquid remained. Hexane was added, causing the formation of a green precipitate. Using a cannula containing a small glass filter, the mother liquor was removed. To the remaining green solid some drops of CH_2Cl_2 and cold hexane were added. This procedure was repeated until no more free bisaminoarene ligand could be detected by ^{1}H NMR spectroscopy. Yield: 0.0280 g (30 μmol, 39%). Anal. Calcd (Found) for C 69.37 (69.94), H 5.15 (5.20), P 10.32 (10.26). Transcyclometalation of **3** with (*S,S*)-**6b** resulted in the formation of (*S,S*)-**7b**. With help of the spectroscopic analyses of (*S,S*)-**7b** the signals resulting from *meso*-**7b** in the mixture obtained by the direct cyclometalation were unequivocally assigned.

(*S,S*)-7b. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.73 (t, ^3J(HH) = 7.4 Hz, 3H, CH_3), 0.80−1.0 (m, 2H, CH_2), 1.00 (t, ^3J(HH) = 6.0 Hz, 3H, CH_3), 1.50−1.70 (m, 3H C*H*-Et, CH_2), 4.05−4.15 (m, 1H, C*H*-Et), 6.21 (vt, ^{vt}J = 8.4 Hz, 2H, *o*-PPh_2), 6.53 (m, 2H, *m*-PPh_2), 6.62 (d, J(HH) = 6.9 Hz, 1H), 6.78−7.00 (m, 6H, *o*-PPh_3), 7.20−7.80 (m, 9H, *m,p*-PPh_3), 8.25−8.32 (m, 2H, *o*-PPh_2). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 13.45 (d, ^3J(CP) = 12.2 Hz, CH_3), 15.87 (d, ^3J(CP) = 8.5 Hz, CH_3), 22.54 (d, ^2J(CP) = 7.4 Hz, CH_2), 23.62 (d, ^2J(CP) = 7.4 Hz, CH_2), 47.66 (d, ^1J(CP) = 21.1 Hz, CH), 52.15 (d, ^1J(CP) = 28.1 Hz, CH), 121.80 (t, J(CP) = 8.5, CH), 122.21 (s, CH), 122.30 (s, CH), 122.54 (d, J(CP) = 15.9 Hz, CH), 123.57 (d, J(CP) = 17.1 Hz, CH), 127.16 (d, ^3J(CP) = 9.7 Hz, *m*-PPh_3), 127.18 (d, ^3J(CP) = 10.4 Hz, *m*-PPh_3), 128.27−134.50 (m), 134.75 (d, ^2J(CP) = 10.9 Hz, *o*-PPh_3), 137.30 (dt, ^1J(CP) = 47.6 Hz, ^3J(CP) = 2.4 Hz, C_{quat} PPh_3), 154.99 (d, J(CP) = 14.6 Hz, C_{quat}), 155.37−155.61 (m, C_{quat}), 173.21 (d, ^1J(CP) = 20.2 Hz, Ru−C_{ipso}). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 38.04 (dd, ^2J(PP) = 19.8 Hz, ^2J(PP) = 254.4 Hz, 1P, PPh_2), 55.06 (dd, ^2J(PP) = 48.0 Hz, ^2J(PP) = 254.4 Hz, 1P, PPh_2), 79.81 (dd, ^2J(PP) = 19.8 Hz, ^2J(PP) = 48.0 Hz, 1P, PPh_3).

(*meso*)-7b. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.06 (t, ^3J(HH) = 7.4 Hz, 6H, CH_3), 1.50−1.70 (m, 2H, CH_2), 1.75−1.90 (m, 2H, CH_2), 2.41−2.50 (m, 2H, C*H*-Et), 6.78−7.80 (aromatic). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 16.10 (vt, ^{vt}J(CP) = 4.0 Hz, CH_3), 25.56 (vt, ^{vt}J(CP) = 3.0 Hz, CH_2), 47.47 (vt, ^{vt}J(CP) = 13.4 Hz, CH), 121.80 (t, J(CP) = 8.5, CH), 122.21 (s, CH), 122.30 (s, CH), 122.54 (d, J(CP) = 15.9 Hz, CH), 123.57 (d, J(CP) = 17.1 Hz, CH), 127.16 (d, ^3J(CP) =9.7 Hz, *m*-PPh_3), 127.48 (d, ^3J(CP) = 9.7 Hz, *m*-PPh_2), 128.27−134.50 (m), 134.67 (d, ^2J(CP) = 9.7 Hz, *o*-PPh_3), 136.20 (dt, ^1J(CP) = 50.0 Hz, ^3J(CP) = 2.4 Hz, C_{quat} PPh_3), 155.37−155.61 (m, C_{quat}), 171.94 (d, ^1J(CP) = 17.7 Hz, Ru−C_{ipso}). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 55.03 (d, ^2J(PP) =32.4 Hz, 2P, PPh_2), 77.73 (t, ^2J(PP) = 32.4 Hz, 1P, PPh_3).

Synthesis of $C_6H_3(CH_2PPh_2)_2$-3,5-Me_3Si-1 (8). To a solution of 1-$C_6H_3(CH_2PPh_2)_2$-3,5-Br-1 (1.11 g, 2 mmol) in diethyl ether (30 mL) at −78 °C was slowly added 2.1 equiv of *t*-BuLi. After stirring for 30 min, an excess of trimethylsilyl chloride was added (2 mL, 15.8 mmol). After 5 h, the resulting mixture was allowed to warm to room temperature. All volatiles were removed in vacuo. The oily residue was treated with degassed water (10 mL) and extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed once with degassed water (10 mL) and then dried over $MgSO_4$. Filtration of insoluble material and removal of the ether under reduced pressure resulted in a colorless waxlike material. Yield: 1.02 g (93%). Anal. Calcd (Found) for C 76.89 (76.66), H 6.64 (6.57), P 11.33 (11.18). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.07 (s, 9H, $SiCH_3$), 3.38 (s, 4H, CH_2), 6.77 (s, 2H, SiCCH), 7.02 (s, 1H, CH *ortho* to both CH_2PPh_2 groups), 7.20−7.60 (m, 20H, PPh_2 aromatic protons). ^{13}C NMR (50 MHz, $CDCl_3$): δ −1.12, (s, CH_3), 36.01 (d, ^1J(CP) = 16.20 Hz, CH_2), 128.41 (d, ^2J(CP) = 6.5 Hz, *o*-PPh_2), 128.73 (s, *p*-PPh_2), 131.00 (t, ^3J(CP) = 6.6 Hz, CH *ortho* to both CH_2PPh_2 groups), 132.13 (m, *C*-CH_2P), 133.10 (d, ^3J(CP) = 18.4 Hz, *m*-PPh_2), 136.41 (dd, ^3J(CP) = 5.7 Hz, ^5J(CP) = 1.7 Hz, SiC*C*H), 138.40 (d, ^1J(CP) = 15.7 Hz, P−C_{quat}), 139.92 (s, Si−C). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −9.11 (s).

Synthesis of $[RuCl(C_6H_2\{CH_2PPh_2\}_2$-2,6-$Me_3Si$-4)$(PPh_3)]$ (9). A solution of **8** (0.43 g, 0.78 mmol) in THF (10 mL) was added to a boiling THF (20 mL) solution of **3** (0.49 g, 0.79 mmol) and heated to reflux for 8 h. The final product was contaminated with a small amount (<5%) of **10**. Yield: 0.51 g (70%). Mp: 135−145 °C (decomp). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.33 (s, 9H, Si−CH_3), 2.45 (m, 2H, CH_2), 3.50 (m, 2H, CH_2), 6.50−8.00 (m, 37H, aromatic protons). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 1.00 (s, Si−CH_3), 40.49 (t, ^1J(CP) = 15 Hz, CH_2), 128.77 (d, J(CP) = 10 Hz), 129.59 (t, J(CP) = 19.1 Hz), 129.92 (t, J(CP) = 4.2 Hz), 130.27 (t, J(CP) = 4.3 Hz), 130.5−131.0 (m), 131.65 (s), 133.5−134.0 (m), 134.1−135.0 (m), 135.99 (d, J(CP) = 10.4 Hz), 136.2−138.5 (m), 152.31 (t, J(CP) = 9.3 Hz), 176.74 (d, J(CP) = 17.2 Hz, Ru−C_{ipso}). ^{31}P{^{1}H} NMR (81 MHz, CD_2Cl_2): δ 36.98 (d, ^2J(PP) = 31.8 Hz, 2P, PCP), 82.73 (t, ^2J(PP) = 31.8 Hz, 1P, PPh_3).

Synthesis of $C_6H_3(CH_2PPh_2)_2$-1,3-D-2 (11-D). To a solution of $C_6H_3(CH_2Br)_2$-1,3-D-2[36] in xylene was added 2 equiv of Et(O)PPh_2. After 2 h of reflux, the volatiles were removed, and the remaining residue was extracted with hexane, resulting in the formation of the corresponding phosphine oxide as a white solid. The reduction was performed by adding $HSiCl_3$ dropwise to a hot solution of the phosphine oxide in benzene. The volatiles were removed in vacuo, and the oily residue was treated with hexane to induce crystallization. The resulting white waxlike precipitate was filtered off and dried under vacuum. Yield: 70% (based on $C_6H_3(CH_2Br)_2$-1,3-D-2).

Even though the synthesis of $C_6H_4(CH_2PPh_2)_2$-1,3 (**11**) was reported some time ago, the available NMR data are incomplete. With the help of one- and two-dimensional NMR techniques, all protons and carbons were located both for $C_6H_4(CH_2PPh_2)_2$-1,3 (**11**) and for its analogue **11**-D. Due to the obvious similarity between these two compounds, we will describe only the NMR data of the former. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.41 (s, 4H, CH_2), 6.89 (m, 2H, CH-4,6), 7.09 (bs, 1H, CH-2), 7.06 (t, ^3J(HH) = 8.3 Hz, 1H, CH-5), 7.38 (m, *m*-PPh_2), 7.44 (m, *p*-PPh_2), 7.48 (m, *o*-PPh_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 35.89 (d, ^1J(CP) = 16.2 Hz, CH_2), 126.99 (m, CH-4,6), 128.12 (s, CH-5), 128.34 (d, ^3J(CP) = 7.1 Hz, *m*-PPh_2), 128.65 (s, *p*-PPh_2), 130.46 (t, ^3J(CP) = 7.1 Hz, CH-2), 132.90 (d, ^2J(CP) = 18.2 Hz, *o*-PPh_2), 137.33 (dd, ^2J(CP) = 8.1 Hz, ^4J(CP) = 2.1 Hz, C-1,3), 138.33 (d, ^1J(CP) = 15.3 Hz, P−C_{quat}). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ −9.52 (s).

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