Articles

Planar-to-Axial Chirality Relay in Phospharuthenocenes. A Rotationally Hindered 2-(2′-Diphenylphosphinonaphth-1′-yl)phospharuthenocene

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Competing steric pressures within the coordination sphere of 2-(2′-X-naphth-1′-yl)-3,4-dimethyl-5-phenyl-η^5-phospholyl(pentamethylcyclopentadienyl)ruthenium(II) complexes (X = OMe (**1**), OH (**3**), OTf (**4**), $PPh_2(O)$ (**5**), PPh_2 (**6**)) give rise to a well-defined and predictable axial chirality about the phospharuthenocene−naphthyl bond. Crystal structure analysis of the platinum complex *cis*-[Pt(**6**)Cl_2] (**7**) shows a very different geometry from that found in *cis*-[Pt(**1**)(PEt_3)Cl_2] (**2**) because of the leverage exerted on the Pt coordination sphere by the (2′-PPh_2-naphth-1′-yl) functionality.

Introduction

The development of functionalized metallocene-based "pseudobiaryl" ligands, which can be used as replacements for more classical biaryl ligand systems,[1] has been treated in some depth recently. Eyecatching examples include Johannsen's MOPF class[2−6] and DMAP analogues,[7] Weissensteiner's Walphos ligands,[8] and Knochel's series (e.g., ferrocenylQuinap)[9,10] derived from the Kagan sulfoxide[10,11] (Figure 1).

Rather than using classical metallocenes, we and others have been interested for some time in exploring the potential for building ligands around phosphametallocene (phosphacyclopentadienyl, Figure 2) complexes,[12] so as to exploit the unusual coordination properties of the sp^2-hybridized phosphorus atom.

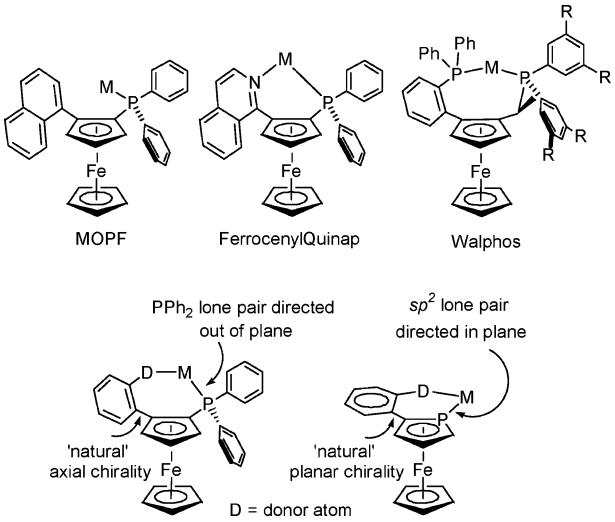

Figure 1. Above: Some pseudobiaryl ligands. Below: Potential influence of the relative positions of the metal and the five-membered ring plane on the nature of the chirality in flexible structures.

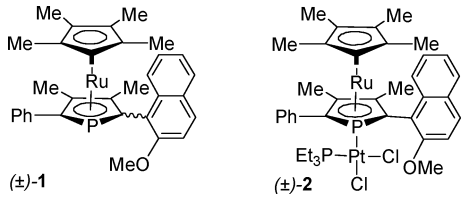

Figure 2.

The preparation of axially chiral ligands constitutes an obvious goal.[13] Conferring useful axial chirality upon classically functionalized metallocenes is usually quite straightforward; the presence of a functional group having a lone pair that will generally be oriented away from the cyclopentadienyl plane (e.g., $-PPh_2$) reinforces the natural tendency of flexible ligands

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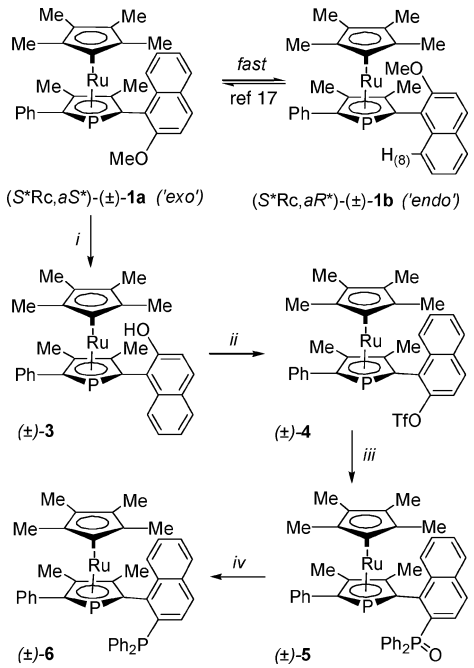
to adopt an axially chiral motif (Figure 1).[4] However, if the lone pair lies in the plane of the five-membered ring, as in a donor heterometallocene, any second coordinating functionality in a nonrestrained system is likely to be drawn toward the ring plane, with the result that the default geometry will often be closer to simple planar chirality.[14,15] For ligands containing heterometallocene and related functionalities, it may therefore be beneficial to incorporate structural elements that actively promote axial chirality, should this be desired.[16]

As part of an investigation into this area, we recently described the synthesis and *tropos* characteristics of the naphthyl-substituted phospharuthenocene **1**, along with its incorporation into specimen platinum complexes **2** (Figure 2).[17]

A number of elements within its coordination sphere suggest that **1** should be a good source of axially chiral phospharuthenocenes.[18] It shows a surmountable maximum in the coplanar configuration {$\Delta G^*_{endo\rightarrow exo}$ 77(1) kJ mol^{-1}}, which results from nonbonding interactions between the naphthyl ring and the 3-methyl group, and also exhibits further nonbonding interactions between the naphthyl and Cp* groups. Solutions of **1** exist as equilibrating (*S**$_{Rc}$,*aS**)-(±)-*exo* and (*S**$_{Rc}$,*aR**)-(±)-*endo* conformers[19] (Scheme 1) because the naphthyl component has similar spatial requirements in each orientation, but increasing the volume of the group in the naphthyl 2-position will obviously destabilize the *endo* form (Figure 3). With the coplanar configuration also disfavored, this should generate an *exo*

Scheme 1. Synthesis of Ligand 6[a]



[a] Reagents and Conditions: *i*: $LiPPh_2$ (3 equiv), THF, 80 °C, 5 h, 87%. *ii:* 4-Nitrophenyltriflate (1.2 equiv), K_2CO_3 (4 equiv), 18C6 (2 equiv), THF, 12 h. 73%. *iii:* $Ph_2P(O)H$ (1.5 equiv), $NaHCO_3$ (2 equiv), $Pd(OAc)_2$ (0.2 equiv), dppp (0.2 equiv), DMSO, 80 °C, 3 h, 72%. *iv:* $(MeHSiO)_n$ (100 equiv), $Ti(OiPr)_4$ (1.5 equiv), THF, 66 °C, 4 h, 93%.

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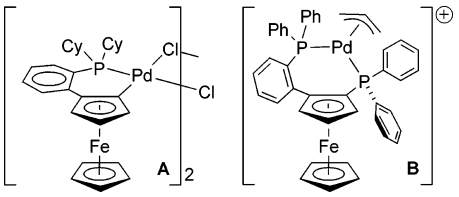

In more general terms, compare the near-coplanarity of the oxazoline imine and phenyl functionalities in the structures of PHOX ligands at group 10 metal centers: Schaffner, S.; Macko, L.; Neuburger, M.; Zehnder, M. *Helv. Chim. Acta* **1997**, *80*, 463−471. Lloyd-Jones, G. C.; Butts, C. P. *Tetrahedron* **1998**, *54*, 901−914. Liu, S. Y.; Muller, J. F. K.; Neuburger, M.; Schaffner, S.; Zehnder, M. *J. Organomet. Chem.* **1997**, *549*, 283−293. Bray, K. L.; Butts, C. P.; Lloyd-Jones, G. C.; Murray, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1421−1422. Schaffner, S.; Muller, J. F. K.; Neuburger, M.; Zehnder, M. *Helv. Chim. Acta* **1998**, *81*, 1223−1232. Blacker, A. J.; Clarke, M. L.; Loft, M. S.; Mahon, M. F.; Williams, J. M. J. *Organometallics* **1999**, *18*, 2867−2873. Lee, S.; Lim, C. W.; Song, C. E.; Kim, K. M.; Jun, C. H. *J. Org. Chem.* **1999**, *64*, 4445−4451. Gomez, M.; Jansat, S.; Muller, G.; Panyella, D.; van Leeuwen, P.; Kamer, P. C. J.; Goubitz, K.; Fraanje, J. *Organometallics* **1999**, *18*, 4970−4981. Blacker, A. J.; Clarke, M. L.; Loft, M. S.; Mahon, M. F.; Humphries, M. E.; Williams, J. M. J. *Chem.−Eur. J.* **2000**, *6*, 353−360. Bernardinelli, G. H.; Kundig, E. P.; Meier, P.; Pfaltz, A.; Radkowski, K.; Zimmermann, N.; Neuburger-Zehnder, M. *Helv. Chim. Acta* **2001**, *84*, 3233−3246. Kollmar, M.; Goldfuss, B.; Reggelin, M.; Rominger, F.; Helmchen, G. *Chem.−Eur. J.* **2001**, *7*, 4913−4927. Vazquez, J.; Goldfuss, B.; Helmchen, G. *J. Organomet. Chem.* **2002**, *641*, 67−70. Zehnder, M.; Neuburger, M.; Schaffner, S.; Jufer, M.; Plattner, D. A. *Eur. J. Inorg. Chem.* **2002**, 1511−1517. Kollmar, M.; Steinhagen, H.; Janssen, J. P.; Goldfuss, B.; Malinovskaya, S. A.; Vazquez, J.; Rominger, F.; Helmchen, G. *Chem.−Eur. J.* **2002**, *8*, 3103−3114. Zehnder, M.; Schaffner, S.; Neuburger, M.; Plattner, D. A. *Inorg. Chim. Acta* **2002**, *337*, 287−298. Kollmar, M.; Helmchen, G. *Organometallics* **2002**, *21*, 4771−4775. Masui, D.; Ohnuki, M.; Yamaguchi, M.; Yamagishi, T. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2003**, *59*, M487−M490. Pican, P.; Gaumont, A. C. *Chem. Commun.* **2005**, 2393−2395. Armstrong, P. B.; Bennett, L. M.; Constantine, R. N.; Fields, J. L.; Jasinski, J. P.; Staples, R. J.; Bunt, R. C. *Tetrahedron Lett.* **2005**, *46*, 1441−1445. Tang, X. B.; Zhang, D. H.; Jie, S. Y.; Sun, W. H.; Chen, J. T. *J. Organomet. Chem.* **2005**, *690*, 3918−3928 with the highly pronounced axial chirality of biphep complexes: Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2000**, *19*, 1567−1571, Tudor, M. D.; Becker, J. J.; White, P. S.; Gagne, M. R. *Organometallics* **2000**, *19*, 4376−4384. Becker, J. J.; White, P. S.; Gagne, M. R. *J. Am. Chem. Soc.* **2001**, *123*, 9478−9479. Mikami, K.; Aikawa, K.; Yusa, Y. *Org. Lett.* **2002**, *4*, 95−97. Mikami, K.; Aikawa, K.; Yusa, Y.; Hatano, M. *Org. Lett.* **2002**, *4*, 91−94. Aikawa, K.; Mikami, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 5458−5461. Mikami, K.; Kakuno, H.; Aikawa, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7257−7260 containing the same metals (data as available from CCDC on 10/25/2006).

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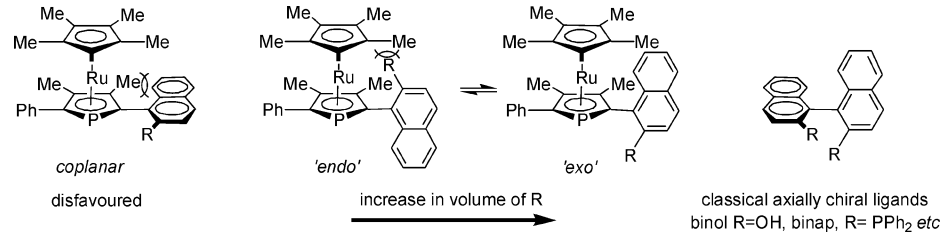

Figure 3. Projected effect of increasing R-group volume in *tropos*-type naphthalene-substituted sandwich complexes.

conformer wherein competing steric pressures provide a more rigid and controlled axial chirality than is available in metallocene-derived ligands having less encumbered substitution schemes. This approach is developed here through the synthesis of the configurationally restricted phosphametallocene phosphine ligand **6**, whose geometry is confirmed in the crystal structure of the platinum complex **7**.

The preparation of **6** is easily effected from compound **1** according to the protocol given in Scheme 1. While the elementary steps are classical, some of the reagents are less so. Oxidation reactions appeared to prevent access to naphthol **3** by a number of methods[20−22] that are routinely employed for the demethylation of aryl methyl ethers (TMSI,[23,24] $Me_2S\cdot BCl_3$[25]), but the compound could be prepared essentially quantitatively under reducing conditions using lithium diphenylphosphide.[26,27] Attempted triflation of **3** under standard conditions (Tf_2O, DMAP[28] or pyridine,[29,30] THF or THP) also failed, apparently because of competing solvent ring-opening when the reaction was performed in THF and very sluggish reactivity in THP; however, good isolated yields of **4** (73%) were obtained through the S_N2 reaction of the corresponding potassium naphtholate with 4-nitrophenyltriflate.[31,32] The phosphorus center was installed very smoothly using $Ph_2P(O)H$ under Hayashi−Morgans conditions,[29,33] in a reaction that proved much faster than in the case reported for Quinap,[34] possibly because of precoordination of the Pd(0) center to the sp^2 phosphorus atom. Finally, reduction of **5** was effected using a polymethyl-hydrosiloxane/Ti(O*i*Pr)$_4$ protocol,[35,36] which proved far superior to $NEt_3/SiHCl_3$-based methods. Nonetheless, the duration of the reaction had to be controlled carefully so as to avoid a rapid decomposition, which set in after complete conversion into **6** had been achieved.[37] For optimum results, the reaction was followed *in situ* by ^{31}P NMR and halted after 95% conversion.

The stereochemistry of naphth-1-ylmetallocenes can be investigated conveniently by NMR spectroscopy because the strong ring currents experienced by the naphthyl-8 proton in *exo* structures provoke a significant high-frequency shift relative to the *endo* form[4,38] (for a definition of the naphthyl-8 proton see **1b** in Scheme 1; typical shifts are $\delta_{H8} = 9.86$ in **1a**, 8.00 ppm in **1b** {C_6D_6}).[17] Compounds **3**−**6** each show only one conformer in solution within the limits of detection by ^{31}P and ^1H NMR spectroscopy. These were subjected to COSY, HSBC, and HSQC analyses, which provided unambiguous identifications of the 8-H protons and allowed definitive configurational assignments to be made in each case. The highly deshielded protons found in compounds **4**, **5**, and **6**, ($\delta^1H = 9.79$, 9.66, and 9.39 ppm for H-8 in C_6D_6, respectively) lie close to the value in the crystallographically established **1a** and confirm *exo* conformations. However, the chemical shift ($\delta^1H = 7.54$ ppm in $CDCl_3$) for H-8 in **3**, containing the smaller OH substituent, clearly indicates an *endo* configuration, and this was confirmed for the solid state by a crystal structure analysis (Figure 4).[39] The atypical reactivity observed during the triflation reaction therefore probably reflects the inaccessible position of the OH functionality, which is embedded within the core of the metallocene. The data also show that the relative bulk of the naphthyl substituent {OH < MeO < TfO < $PPh_2(O)$} correlates broadly with the disappearance of the *endo* form (OH > MeO > TfO, $PPh_2(O)$), in accordance with the proposed model wherein the handedness of the axial chirality is governed primarily by hindrance that drives the naphthyl group through the phospholyl plane into the lowest energy configuration.

The overall outcome of the opposing steric effects in the phospharuthenocenephosphine **6** is not obvious *ab initio*, but its formulation as a ligand having pronounced axial chirality was confirmed through an X-ray analysis of its complex at a $PtCl_2$ center, **7** (eq 1, Figure 5).

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(37) This effect has precedent in MOPF chemistry; see ref 4.
(38) Note that half-sandwich binap-derived 2-diphenylphosphinonaphthalen-1-yl groups do not show 8-H protons outside the normal aromatic range: Geldbach, T. J.; Pregosin, P. S. *Eur. J. Inorg. Chem.* **2002**, 1907−1918. Geldbach, T. J.; den Reijer, C. J.; Worle, M.; Pregosin, P. S. *Inorg. Chim. Acta* **2002**, *330*, 155−160. Geldbach, T. J.; Pregosin, P. S.; Albinati, A. *Organometallics* **2003**, *22*, 1443−1451. Geldbach, T. J.; Breher, F.; Gramlich, V.; Kumar, P. G. A.; Pregosin, P. S. *Inorg. Chem.* **2004**, *43*, 1920−1928. Geldbach, T. J.; Pregosin, P. S.; Rizzato, S.; Albinati, A. *Inorg. Chim. Acta* **2006**, *359*, 962−969. Equally, the lack of a highly deshielded ^1H proton resonance in Knochel's "ferrocenylquinap" may provide a clue as to its performance difference[10] with respect to Quinap itself.
(39) The structure can be compared with the phosphaferrocene homologue where, unlike in **3**, the hydrogen of the OH functionality is oriented away from the metal center.[17] Thus the electronic stabilization resulting from the O-H···Ru interaction is probably small. For a related system, see: Paley, R. S.; Estroff, L. A.; McCulley, D. J.; Martinez-Cruz, L. A.; Sanchez, A. J.; Cano, F. H. *Organometallics* **1998**, *17*, 1841−1849. For a theoretical analysis of this kind of interaction: Vrcek, V.; Buhl, M. *Organometallics* **2006**, *25*, 358−367, and references therein.

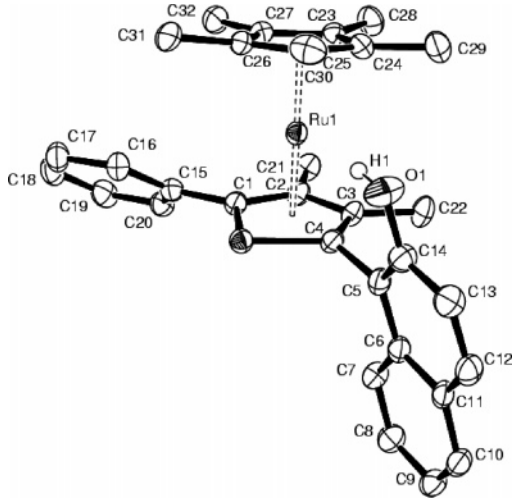
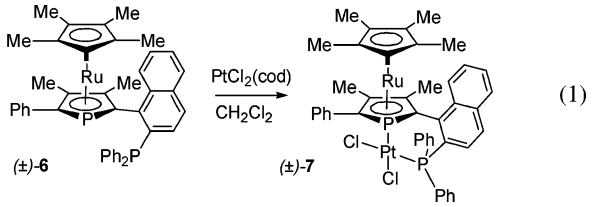


Figure 4. Molecular structure of **3**. Distances (Å): Ru(1)−P(1), 2.4192(5); Ru(1)−C(1), 2.221(2); Ru(1)−C(2), 2.192(2); Ru(1)−C(3), 2.201(2); Ru(1)−C(4), 2.254(2); Ru(1)−C(23), 2.198(2); Ru(1)−C(24), 2.205(2); Ru(1)−C(25), 2.224(2); Ru(1)−C(26), 2.204(2); Ru(1)−C(27), 2.186(2); P(1)−C(1), 1.791(2); P(1)−C(4), 1.787(2); C(1)−C(2), 1.437(3); C(2)−C(3), 1.437(3); C(3)−C(4), 1.420(3); C(4)−C(5), 1.494(2); C(1)−C(15), 1.482(3). Angles (deg): phospholyl−C(4)−C(5), 10.6; intersection of best phospholyl and naphthyl planes: 78.2.



(1)

Two features stand out. The first is the angle defined by the best phospholyl and naphthyl group planes (54.5°), which, although significant, lies toward the low end of the range for normal biaryl-type structures in platinum complexes.[40] The second is the localization of the platinum atom well above the best phospholyl plane (by 1.06 Å, phospholyl centroid−P−Pt = 149.0° for **7**; compare to 0.62 Å, phospholylcentroid−P−Pt = 161.8° for **2**). This combination of effects provokes an unusual PPh_2 geometry wherein the face-oriented equatorial aryl has its C_2-axis lying essentially coplanar with the best plane about the platinum atom, and the edge-on axial phenyl group is tilted in a fashion that orients the *para* carbon (C26) closer to the plane passing through the Pt and bisecting the two chlorine atoms than the *ipso* carbon (C23).

The parameters about platinum in **7** are compared with those found in the related complex containing a methoxynaphthyl substituent (**2**) in Figure 6.[41] The Pt−P{sp^2} and Pt−Cl (*trans* to P{sp^2}) bond lengths are both significantly shorter in **7** than **2**, so that the position of the platinum atom above the phospholyl plane in **7** appears to lessen the p-character in the Pt−P bond with an associated reduction in *trans* influence. The very different metal positions in the two complexes are consistent with the generally held tenet[42,43] that the potential surface for the motion of a metal atom about the sp^2-hybridized phosphorus is relatively flat because of the spherical nature of the lone pair, the implication being that the position of the metal is influenced strongly by the sp^3 phosphorus atom, so that the axial chirality constitutes a dominant structural element within the complex. The modification of the competing steric influences upon the naphthyl lever, through variation of the bulk of the phospholyl 3-substituent, the nature of the cyclopentadienyl ring, and the covalent radius of the metallocene metal center in ligands such as **6** should therefore provide a means of performance optimization. For classical biaryl-based diphosphines (segphos,[44] synphos,[45,46] tunaPhos,[47] etc.[48]) it is widely accepted that a decrease in interplanar angle generally translates into a more intimate ligand−substrate interaction during catalysis and thus better performance; thus, even if the system is very different from those containing the classical biaryls above, the relatively small interplane observed in **6** (compare $PdCl_2$·Segphos: 60.1°,[49] $PdCl_2$·binap: 70.2°[49,50]) suggests a favorable projection of the aryl groups into the metal coordination sphere (Table 1).

The pathways above provide useful phosphametallocene intermediates, and, in utilizing both conformers of **1**, furnish an atom-economical and simple means of relaying the planar chirality of the phosphametallocene into a well-ordered axial chirality about the phospholyl−naphthyl link. Given that a very wide variety of useful C_1-symmetrical ligands have been prepared from naphthyl triflates[51] and that optically pure 2-aryl-substituted phosphametallocenes are, in principle, easy to prepare,[52] this approach promises to provide an attractive and chirally economical route to a variety of enantiopure axially chiral phosphametallocenes.

Experimental Section

All operations were performed either using cannula techniques on Schlenk lines under an atmosphere of dry nitrogen or in a Braun

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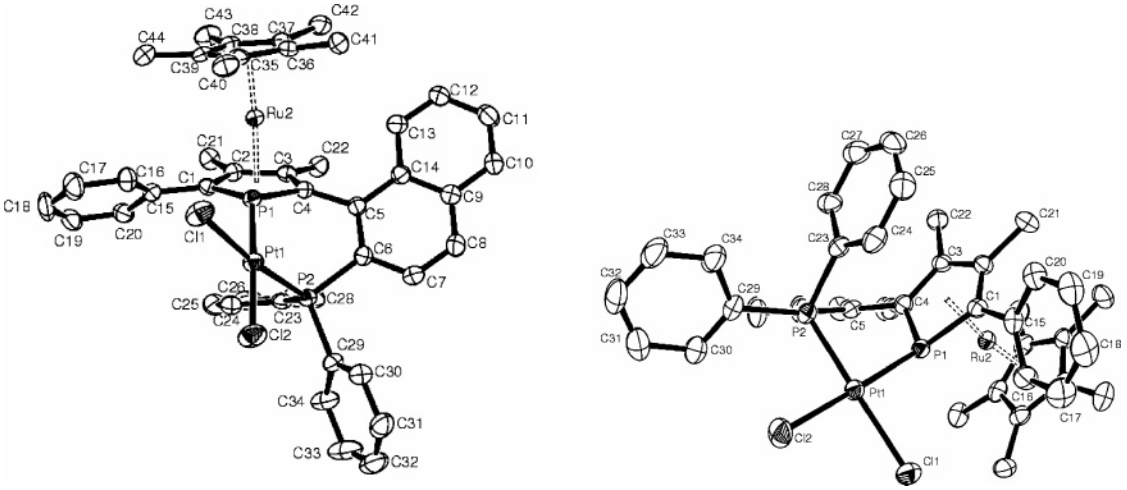

Figure 5. Two views of the molecular structure of **7**. Selected distances (Å): Pt(1)−P(1), 2.203(1); Pt(1)−P(2), 2.242(1); Pt(1)−Cl(2), 2.322(1); Pt(1)−Cl(1), 2.361(1); Ru(2)−C(35), 2.188(4); Ru(2)−C(36), 2.197(4); Ru(2)−C(39), 2.199(4); Ru(2)−C(37), 2.205(4); Ru(2)−C(38), 2.208(4); Ru(2)−C(2), 2.223(4); Ru(2)−C(1), 2.249(4); Ru(2)−C(3), 2.272(4); Ru(2)−P(1), 2.297(1); Ru(2)−C(4), 2.314(4); P(1)−C(4), 1.764(4); P(1)−C(1), 1.768(4); C(1)−C(2), 1.419(5); C(1)−C(15), 1.487(5); C(2)−C(3), 1.451(5); C(3)−C(4), 1.436(5); C(4)−C(5), 1.498(5). Intersection of best phospholyl and naphthyl planes: 54.5°.

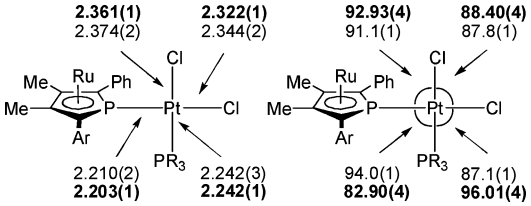

Figure 6. Internuclear separations (Å) and angles (deg) in (±)-**2** (normal text, Ar = 2-methoxynaphth-1-yl, R = Et) and (±)-**7** (bold, Ar, PR_3 = 2-diphenylphosphanylnaphth-1-yl).

Labmaster 130 drybox under dry purified argon. Column chromatography was performed on 63−200 μm silica or 50−160 μm neutral alumina as appropriate. Compound **1** was obtained as described previously.[17] Solvents were distilled under dry nitrogen, THF from sodium-benzophenone ketyl, pentane from sodium-benzophenone ketyl-tetraglyme, diethyl ether from sodium hydride, DMSO from calcium hydride, and dichloromethane from P_4O_{10}. Solvents for chromatography were degassed by bubbling with nitrogen but otherwise used as received. Deuterobenzene was used as received from Eurisotop (Saclay); chloroform and deuterochloroform were deacidified through neutral alumina prior to use. NMR measurements were made on a Bruker Avance 300 spectrometer and are referenced to internal C_6D_5H or $CHCl_3$ and external H_3PO_4 as appropriate. Mass spectra were obtained under 70 eV electron impact or chemical ionization using ammonia on a Hewlett-Packard 5989B spectrometer. Combustion analyses were performed by Marie-Françoise Bricot at the "Service de microanalyse du CNRS", Gif sur Yvette, France.

3: Compound **1** (1.16 g, 2.0 mmol) and Ph_2PLi·2THF (1.34 g, 4.0 mmol, 2 equiv) were dissolved in freeze−thaw cycled THF (75 mL), and the solution was refluxed under monitoring by ^{31}P NMR. After 16 h, the signals due to the reagent **1** (−19.7, −24.8 ppm) had disappeared and were replaced by a peak corresponding to Ph_2PMe (−26 ppm). The solution was hydrolyzed with water (ca. 0.2 mL) and dried over $MgSO_4$. Evaporation to dryness and column chromatography on silica (pentane/CH_2Cl_2, 9:1) gave fast-running bands of Ph_2PMe and Ph_2PH, which were discarded. The product was subsequently eluted in pure CH_2Cl_2 and was obtained as a white solid, which darkened to pale yellow upon exposure to air. Yield: 985 mg (87%).

On a larger scale, the chromatographic step can be avoided through crystallization of the crude reaction hydrolyzate from boiling toluene. In this case, the crystals observed contain one-half mole of toluene of solvation.

Table 1. Summary of Data Pertaining to the Crystal Structures and Refinements of Compounds 3 and 7[a]

	3·0.5C_7H_8	**7**·2CH_2Cl_2
M/Da	611.69	1169.63
space group	$P\bar{1}$	$P2_1/n$
a/Å	8.512(1)	11.315(1)
b/Å	11.989(1)	20.571(1)
c/Å	15.228(1)	19.376(1)
α/deg	110.950(1)	90
β/deg	90.330(1)	98.406(1)
γ/deg	100.160(1)	90
U/Å^3	1424.5(2)	4461.5(5)
Z	2	4
D_c/g cm^{-3}	1.426	1.741
F(000)	634	2304
μ/cm^{-1}	0.634	3.935
h/deg	−11 to 11	−15 to 15
k/deg	−16 to 16	−23 to 28
l/deg	−21 to 21	−27 to 27
size/mm	0.20 × 0.20 × 0.20	0.20 × 0.16 × 0.04
no. of indep reflns	8224	12 988
no. of refined reflns	7206	9412
wR_2 [$I > 2\sigma(I)$]	0.1048	0.1075
R_1	0.0375	0.0418
GOF on F^2	1.019	1.000
max. peak; hole/e Å^{-3}	1.089(0.093); −1.534(0.093)	1.919(0.151); −2.556(0.151)
CCDC entry	629054	629055

[a] All structures were measured and collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation having λ = 0.71070 Å at 150 K. In all cases reflections with intensity >2σ(*I*) were refined on F^2 using direct methods in SHELXL. Full data have been deposited with the Cambridge Crystallographic Data Centre and can be obtained free from www.ccdc.cam.ac.uk/conts/retrieving.html.

^{31}P NMR ($CDCl_3$): δ −35.1. ^1H NMR ($CDCl_3$): δ 8.51 (d, J_{PH} = 1.4 Hz, 1H, OH), 7.73 (d, J_{HH} = 7.4 Hz, 1H, 5-Np), 7.68 (d, J_{HH} = 8.9 Hz, 1H, 4-Np), 7.54 (d, J_{HH} = 8.5 Hz, 1H, 8-Np), 7.37 (Ψt, J_{HH} = 7 Hz, 1H, 7-Np), 7.36 (Ψd, J_{HH} = 8, J_{HH} = 7.5 Hz, 1H, 6-Np), 7.19 (d, J_{HH} = 8.9 Hz, 1H, 3-Np), 7.17 (Ψt, J_{HH} = 7.5 Hz, 1H, *p*-Ph), 2.27 (s, 3H, *Me*CCPh), 1.75 (s, 15H, Cp*), 1.65 (s, 3H, *Me*CCNp). ^{13}C NMR ($CDCl_3$): δ 150.2 (d, J_{PC} = 2.0 Hz, 2-Np), 138.7 (d, J_{PC} = 16.9 Hz, *i*-Ph), 133.6 (d, J_{PC} = 2.2 Hz, 8a-Np), 129.1 (d, J_{PC} = 8.2 Hz, *o*-Ph), 128.7 (4a-Np), 128.6 (4-Np), 128.3 (5-Np), 127.9 (m-Ph), 126.1 (7-Np), 125.9 (*p*-Ph), 125.2 (8-Np), 122.6 (6-Np), 117.3 (3-Np), 113.2 (d, J_{PC} = 13.7 Hz, 1-Np),

102.3 (d, J_{PC} = 59.9 Hz, P*C*Ph), 97.2 (d, J_{PC} = 3.5 Hz, PC*C*Me), 93.7 (d, J_{PC} = 58.5 Hz, P*C*Np), 92.0 (d, J_{PC} = 4.1 Hz, PC*C*Me), 89.4 (Cp*), 13.8 (*Me*CCPh), 13.6 (*Me*CCNp), 10.4 (MeCp*). Anal. Calcd for $C_{32}H_{33}OPRu$ (**3**·1/2C_7H_8): C, 69.7; H, 6.10. Found: C, 70.12; H, 6.04. EI-MS (*m*/*z*, %): 566, 100.

4: Compound **3** (100 mg, 0.177 mmol), anhydrous potassium carbonate (49 mg, 0.35 mmol, 2 equiv), 18C6 (183 mg, 3.9 equiv), and 4-nitrophenyltriflate (54.3 mg, 1.13 equiv) were dissolved in THF (10 mL), and the mixture was stirred at room temperature for 12 h. Excess potassium chloride (ca. 50 mg) was then added, and the solvent was removed under reduced pressure. The crude mixture was taken up in dichloromethane (5 mL) and washed with NaOH (10% aq, 15 mL) and water (2 × 15 mL) to eliminate 4-nitrophenolate prior to drying over anhydrous magnesium sulfate. After filtration and removal of solvents under reduced pressure, the mixture was purified by chromatography on silica (pentane/CH_2Cl_2, 4:1), whereupon the product was eluted as a yellow band (90 mg, 73%). Recrystallization from MeOH/Et_2O gave an analytically pure sample.

^{31}P NMR (C_6D_6): δ −20.8. ^{1}H (C_6D_6): δ 9.79 (d, J_{HH} = 8.8 Hz, 1H, 8-Np), 7.52−7.45 (m, 2H, 5-Np and 7-Np), 7.44 (Ψd, J_{HH} = 8 Hz, 2H, *o*-Ph), 7.28 (d, J_{HH} = 9.1 Hz, 1H, 4-Np), 7.27 (m, 1H, 6-Np), 7.18 (d, J_{HH} = 9.1 Hz, 1H, 3-Np), 7.15 (Ψt, J_{HH} = 8 Hz, 2H, *m*-Ph), 7.05 (Ψt, J_{HH} = 8 Hz, 1H, *p*-Ph), 2.07 (s, 3H), 2.00 (s, 3H), 1.48 (s, 15H, Cp*). ^{13}C NMR (C_6D_6): 145.6 (d, J_{P-C} = 3.4 Hz, 2-Np), 139.2 (d, J_{P-C} = 17.6 Hz, *ipso*-Ph), 133.3 (4a-Np), 132.0 (8a-Np), 130.1 (d, J_{P-C} = 14.6 Hz, 1-Np), 129.8 (d, J_{P-C} = 7.6 Hz, *o*-Ph), 128.8 (d, J_{P-C} = 8.9 Hz, *8-Np*), 128.6 (4-Np, 5-Np, or 7-Np), 128.3 (4-Np, 5-Np, or 7-Np), 128.2 (4-Np, 5-Np, or 7-Np), 127.0 (6-Np), 126.2 (p-Ph), 126.0 (5-Np or 7-Np), 120.0 (3-Np), 119.2 (q, J_{F-C} = 321 Hz, *C*F_3), 104.2 (d, J_{P-C} = 59.6 Hz, P*C*CPh), 94.5 (d, J_{P-C} = 62.5 Hz, P*C*CNp), 93.9 (d, J_{P-C} = 4.0 Hz, PC*C*), 92.7 (d, J_{P-C} = 3.9 Hz, PC*C*), 88.9 (Cp*), 14.6, 13.4, 10.6 (Cp*). CI-MS (+ve NH_3) (*m*/*z*, %): 699 ([M + H]$^+$, 100), 566 (M + H − CF_3SO_2, 10%). Anal. Calcd for $C_{33}H_{32}F_3O_3PRuS$: C, 56.81; H, 4.62. Found: C, 56.76; H, 4.56.

5: Compound **4** (140 mg, 0.20 mmol) was added to a mixture containing 1,3-bis(diphenylphosphino)propane (16.8 mg, 0.041 mmol, ca. 20 mol %), freshly prepared diphenylphosphineoxide (158.2 mg, 0.78mmol), yellow palladium acetate (28 mg, 0.041 mmol), and sodium hydrogen carbonate (98 mg, 1.17 mmol, 6 equiv) in freshly distilled DMSO (10 mL). The solution was heated to 85 °C for 1.5 h, whereupon ^{31}P NMR showed the complete disappearance of the starting triflate **4**. CH_2Cl_2 (50 mL) was added, and the organic phase was washed with brine (2 × 50 mL), saturated aqueous sodium carbonate (50 mL), and again brine (50 mL). After drying over anhydrous sodium sulfate, the dichloromethane was removed under reduced pressure and the oily, red crude product was purified by chromatography on silica gel. After a short period of washing the column with pentane/dichloromethane (1:1) the product was eluted as a broad yellow band using a gradient of pentane/ethyl acetate (8:2 rising to 7:3). Removal of the solvent under reduced pressure gave a yellow solid (110 mg, 72%).

^{31}P NMR ($CDCl_3$): δ 26.7 (sp^3), −13.5 (sp^2). ^{1}H NMR ($CDCl_3$): δ 9.66 (d, J_{HH} = 8.6 Hz, 1H, 8-Np), 7.81 (d, J_{HH} = 7.6 Hz, 1H, 5-Np), 7.70−7.55 (m, 5H, 4-Np, 6-Np, 7-Np, *o*-PhP═O), 7.51−7.30 (m, 6H, 3-Np, *o*-PhP═O, *m*-PhP═O, *p*-PhP═O), 7.22 (Ψt, J_{HH}=7.1 Hz, 2H, *m*-Ph), 7.17−7.05 (m, 6H, *o*-Ph, *p*-Ph, *m*-PhP═O, *p*-PhP═O), 2.03 (s, 6H, *Me*CCP), 1.58 (s, 15H, Cp*). ^{13}C NMR ($CDCl_3$): δ 144.2 (dd, J_{PC} = 14.9 Hz, J_{PC} = 6.9 Hz, 1-Np), 139.3 (d, J_{PC} = 17.3 Hz, *ipso*-Ph), 136.2 (d, J_{PC} = 104.5 Hz, *ipso*-PhP(O)), 134.6 (d, J_{PC} = 2.2 Hz, 4a-Np), 133.6 (d, J_{PC} = 10.4 Hz, *ipso*-PhP(O)), 131.7 (d, J_{PC} = 8.8 Hz, *o*-Ph_2P(O)), 131.4 (d, J_{PC} = 10.9 Hz, 8a-Np), 131.1 (dd, J_{PC} = 104 Hz, J_{PC} = 3.9 Hz, 2-Np), 130.9 (d, J_{PC} = 2.7 Hz, *p*-PhP(O)), 130.8 (*p*-PhP(O)), 130.7 (d, J_{PC} = 13.5 Hz, 3-Np), 129.2 (d, J_{PC} = 8.7 Hz, *o*-Ph), 128.6 (d, J_{PC} = 6.0 Hz, 8-Np), 128.2 (d, J_{PC} = 11.6 Hz, *m*-PhP(O)), 128.1 (d, J_{PC} = 12.1 Hz, *m*-PhP(O)), 127.8 (6-Np), 127.5 (5-Np), 127.4 (*m*-Ph), 125.6 (d, J_{PC} = 13.4 Hz, 4-Np), 125.3 (7-Np), 125.1 (*p*-Ph), 101.7 (dd, J_{PC} = 61.2 Hz, J_{PC} = 5.8 Hz, P*C*Np), 99.8 (d, J_{PC} = 58.3 Hz, P*C*Ph), 98.0 (d, J_{PC} = 3.6 Hz, PC*C*Me), 90.3 (d, J_{PC} = 3.9 Hz, PC*C*Me), 88.5 (Cp*), 15.3 (*Me*CCP), 13.9 (*Me*CCP), 10.6 (MeCp*). CI-MS (+ve NH_3) (*m*/*z*, %): 751, 100. Yellow crystals obtained from slow cooling of a dichloromethane/methanol solution turned opaque upon drying and contain one-half equivalent of methanol. Anal. Calcd for $C_{89}H_{88}O_3P_4Ru_2$ (**5**·1/2MeOH): C, 69.79; H, 5.79. Found: C, 69.83; H, 5.72.

6: Compound **5** (50 mg, 0.066 mmol), poly(methylhydrosiloxane) (400 μL, ca. 7.8 mmol of monomer), and titanium tetra(isopropoxide) (30 μL, 0.11mmol) were mixed in THF (2.5 mL) and heated to reflux for 4 h, whereupon conversion into **6** had reached 95% according to ^{31}P NMR monitoring. The solution was cooled in an ice bath, and aqueous sodium hydroxide solution (2 M, 3 mL) was cautiously added dropwise. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 5 mL). The dichloromethane layers were combined and dried over anhydrous magnesium sulfate. After filtration and removal of dichloromethane under reduced pressure, the product was obtained as a yellow solid (45 mg, 93%), which was sufficiently pure for further use.

^{31}P NMR ($CDCl_3$): δ −5.7 (d, J_{PP} = 38.5 Hz) (sp^3), −19.3 (d, J_{PP} = 38.5 Hz) (sp^2). ^{1}H NMR ($CDCl_3$): δ 9.39 (d, J_{HH} = 8.3 Hz, 1H, 8-Np), 7.77 (dd, J_{HH} = 8.1 Hz, J_{HH} = 1.3 Hz, 1H, 5-Np), 7.62 (d, J_{HH} = 8.4 Hz, 1H, 4-Np), 7.56 (ddd, J_{HH} = 8.3 Hz, J_{HH} = 6.9 Hz, J_{HH} = 1.4 Hz, 1H, 7-Np), 7.56 (ddd, J_{HH} = 8.1 Hz, J_{HH} = 6.9 Hz, J_{HH} = 1.5 Hz, 1H, 6-Np), 7.37−7.22 (m, 10H, Ph), 7.20−7.00 (m, 6H, Ph and 3-Np), 2.09 (s, 3H, *Me*CCP), 1.73 (s, 15H, Cp*), 2.69 (s, 3H, *Me*CCP). ^{13}C NMR ($CDCl_3$): δ 137.1 (dd, J_{PC} = 13.2 Hz, J_{PC} = 6.8 Hz, 1-Np), 135.7 (d, J_{PC} = 10.0 Hz), 134.8 (d, J_{PC} = 1.8 Hz), 132.1 (d, J_{PC} = 13 Hz), 131.7 (d, J_{PC} = 2.6 Hz), 131.3 (d, J_{PC} = 5.9 Hz), 131.2 (d, J_{PC} = 5.7 Hz), 131.0 (d, J_{PC} = 5.9 Hz), 130.9 (d, J_{PC} = 2.5 Hz), 129.5 (dd, J_{PC} = 5.2 Hz, J_{PC} = 3.6 Hz), 128.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.7, 126.7, 125.2, 124.7, 123.9, 124.7 (7-Np), 101.9 (dd, J_{PC} = 56 Hz, J_{PC} = 11.2 Hz, P*C*), 99.8 (d, J_{PC} = 59 Hz, P*C*), 96.3 (dd, J_{PC} = 3.7 Hz, J_{PC} = 3.9 Hz, PC*C*Me), 89.8 (d, J_{PC} = 3.9 Hz, PC*C*Me), 88.4 (Cp*), 14.4 (d, J_{PC} = 12.1 Hz, *Me*CCP), 13.9 (*Me*CCP), 10.8 (MeCp*). CI-MS (+ve NH_3) (*m*/*z*, %): 735, 100.

7: Compound **6** (45 mg, 0.061mmol) was dissolved in chloroform (1 mL) and added to a stirred chloroform (1 mL) solution of [$PtCl_2$-(1,5-cod)] (22.8 mg, 0.061 mmol) at −60 °C. The solution was further stirred for 15 min, warmed to room temperature, and evaporated to dryness under reduced pressure. Crystallization by slow diffusion of methanol (2 mL) into a solution of the crude reaction product dissolved in dichloromethane (0.5 mL) gave compound **7** as fine yellow plates (39 mg, 64%).

^{31}P NMR (CH_2Cl_2): δ 65.7 (J_{PP} = 14.4 Hz, J_{PPt} = 3166 Hz) (sp^3), 36.5 (d, J_{PP} = 14.4 Hz, J_{PPt} = 4207 Hz) (sp^2). ^{1}H NMR ($CDCl_3$): δ 8.21 (d, J_{HH} = 8.7 Hz, 1H, 8-Np), 7.87 (dd, J_{HH} = 8.2 Hz, J_{HH} = 2.7 Hz, 5-Np), 7.77 (d, J_{HH} = 8.85 Hz, 4-Np), 7.59 (ddd, J_{HH} = 7.4 Hz, J_{HH} = 7.4 Hz, J_{HH} = 2.7 Hz, 1H, 6-Np or 7-Np), 7.57 (ddd, J_{HH} = 7.5 Hz, J_{HH} = 7.5 Hz, J_{HH} = 2.2 Hz 6-Np or 7-Np), 7.52−7.19 (m, 15H, Ph), 7.03 (dd, J_{PH} = 10.4 Hz, J_{HH} = 8.8 Hz 1H, 3-Np), 1.78 (s, 15H, Cp*), 1.71 (s, 3H), 1.53 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 137.1 (dd, J_{P-C} = 13.3 Hz, J_{P-C} = 6.8 Hz, 2-Np), 135.7 (d, J_{P-C} = 10.0 Hz), 134.8, 132.1(d, J_{P-C} = 13.0 Hz), 131.7 (d, J_{P-C} = 2.6 Hz), 131.3 (d, J_{P-C} = 5.9 Hz), 131.2 (d, J_{P-C} = 5.7 Hz), 131.0 (d, J_{P-C} = 5.9 Hz), 130.9 (d, J_{P-C} = 2.9 Hz), 129.5 (dd, J_{P-C} = 5.2 Hz, J_{P-C} = 3.6 Hz), 128.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.7, 126.7, 125.2, 124.7, 123.9, 98.9 (d, J_{P-C} = 9.7 Hz, PC*C*), 93.0 (Cp*), 92.2 (d, J_{P-C} = 8.6 Hz, PC*C*),

79.5 (dd, J_{P-C} = 18.6 Hz, J_{P-C} = 18.6 Hz, P*C*), 78.1 (d, J_{P-C} = 21 Hz, P*C*), 14.7(d, J_{P-C} = 3.6 Hz, Me), 13.4 (d, J_{P-C} = 4.2 Hz, Me), 11.2 (Cp*). Anal. Calcd for $C_{46}H_{46}Cl_6P_2PtRu$ (**7**·$2CH_2Cl_2$): C, 47.23; H, 3.96. Found: C, 47.39; H, 4.07.

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Supporting Information Available: Additional crystallographic data and ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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