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# Enantioselective organic syntheses using chiral transition metal complexes V[1]. (2*S*,3*S*)-Bis(dibenzophospholyl)butane, a rigid (*S*,*S*)-CHIRAPHOS analog

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**Abstract**

The P–Ph cleavage of phenyldibenzophosphole (**1**) with lithium in THF gives lithium dibenzophospholide (**2**). Reaction of **2** with ethyleneglycol ditosylate produces the known chelate ligand 1,2-bis(dibenzophospholyl)ethane (**3**) in good yield. Similarly, **2** and (2*R*,3*R*)-butanediol ditosylate give the new chiral chelate ligand (2*S*,3*S*)-bis(dibenzophospholyl)butane (**4**). Ligand exchange of $[CpRu(PPh_3)_2Cl]$ with **3** or **4** yields the halfsandwich complexes $[CpRu(C_{12}H_8PC_2H_4PC_{12}H_8)Cl]$ (**5**) and $[CpRu((S,S)\text{-}C_{12}H_8PCHMeCHMePC_{12}H_8)Cl]$ (**6**). Complex **6** was characterized crystallographically (monoclinic, space group $P2_1$ (no. 4), $a = 820.6(4)$, $b = 1501.0(3)$, $c = 1172.8(6)$ pm, $\beta = 108.87(2)°$, $V = 1.367(1) \times 10^9$ pm$^3$, $Z = 2$). The most conspicuous feature of the structure of **6** is the perfect coplanarity of the two dibenzophosphole moieties imposed by their steric interaction with the Cp ligand. Complex **6** and the thiophene complex $[CpRu((S,S)\text{-}C_{12}H_8PCHMeCHMePC_{12}H_8)(SC_4H_4)]BF_4$ (**7**) derived therefrom are remarkably unreactive with regard to ligand substitutions. A possible explanation is the lack of intramolecular M···H–C stabilization en route to the transition state of ligand substitution. The enantiomeric purity of **6** and **7** could nevertheless be demonstrated by conversion to diastereomerically pure $[CpRu((S,S)\text{-}C_{12}H_8PCHMeCHMePC_{12}H_8)((S)\text{-}CNCHMePh)]BF_4$ (**8**).


*Keywords:* Chiral auxiliaries; Phosphine ligands; Phospholes; Ruthenium

## 1. Introduction

In previous work we have been able to demonstrate that the Lewis acid $[CpRu((S,S)\text{-CHIRAPHOS})]^+$ is a quite effective chiral auxiliary in ligand-based reactions [1–5]. As is the case in enantioselective homogeneous catalysis the 'chiral information' is transmitted by steric interactions between the substituents at the phosphorus atoms and the coordinated substrate molecule [6,7]. From a number of crystal structure determinations of thioether and sulfoxide complexes $[CpRu((S,S)\text{-CHIRAPHOS})L]PF_6$ we had learnt that in these complexes the arrangement of the phenyl groups at phosphorus is quite flexible. This certainly helps accommodate a large variety of substrate molecules L; on the other hand, too large a flexibility of the metal complex might be expected to be detrimental with regard to the degree of asymmetric induction.

Replacing the diphenylphosphino groups of (*S*,*S*)-CHIRAPHOS by dibenzophosphole residues would be a very simple way to make the ligand framework more rigid without at the same time changing its electronic properties. A few examples of bis(dibenzophosphole) chelate ligands have indeed been described in the literature [8–14] including the analogs of dppe [8], DIOP [9] and BDPP [10] (Scheme 1).

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[1] For Part IV, see ref. [1].

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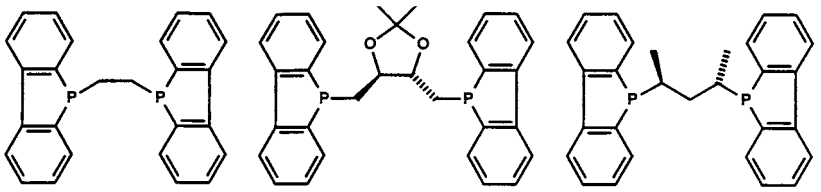


A B C

Scheme 1. Bis(dibenzophosphole) analogs of dppe (A), DIOP (B) and BDPP (C).

## 2. Results

### 2.1. Synthesis

The synthesis of (2*S*,3*S*)-bis(dibenzophospholyl)butane (**4**) and its achiral analog 1,2-bis(dibenzophospholyl)ethane (**3**) is closely analogous to the procedure originally developed by Kagan et al. for the synthesis of the DIOP analog **B** [9] (Scheme 1). Cleavage of phenyldibenzophosphole (**1**) with lithium in THF followed by quenching with *t*-butylchloride gave a solution of lithium dibenzophospholide (**2**). Further reaction with ethyleneglycol ditosylate (Scheme 2) gave 1,2-bis(dibenzophospholyl)ethane (**3**) in good yield as a colorless crystalline compound. Ligand **3** had been synthesized previously by the reaction of 1,2-bis(dichlorophosphino)ethane with 2,2′-dilithiobiphenyl [8]. The procedure outlined here has the advantage of being simpler and more economical.

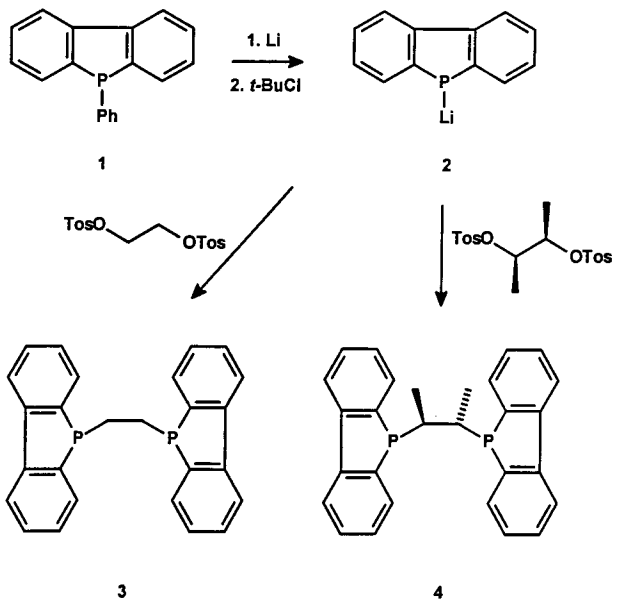
Reaction of the lithium salt **2** with (2*R*,3*R*)-butanediol ditosylate at room temperature (r.t.) gave an almost quantitative yield of the chiral diphosphine **4**. NMR analysis of the crude reaction mixture revealed minor amounts of byproducts among which 1H-dibenzophosphole and the monosubstitution product, $TosOCH(Me)CH(Me)PC_{12}H_8$, could be identified. Nevertheless, even after chromatography the compound could be isolated only as white semi-solid material. This situation is reminiscent of the difficulties encountered in the isolation of (*S*,*S*)-CHIRAPHOS [15]. Instead of attempting a further purification via some labile addition compounds [15], **3** and the crude **4** were reacted with $[CpRu(PPh_3)_2Cl]$ in refluxing toluene. As expected the exchange of $PPh_3$ for the chelate ligand proceeded smoothly [16] giving **5** and **6** in high yields as orange-colored crystalline compounds (Scheme 3). Complexes **5** and **6** have very similar spectroscopic properties, the unsymmetrical structure of **6** is apparent from the non-equivalence of the two phosphorus nuclei which give rise to a well-separated AB system with the typical P–P coupling of 43 Hz.

### 2.2. Molecular structure of $[CpRu(C_{12}H_8PCHMeCHMePC_{12}H_8)Cl]$ (6)

Crystals of **6** suitable for X-ray work were obtained from dichloromethane/hexane. The details of the structure determination are described in the Section 4 and Fig. 1 shows a view of the molecule. The coordination sphere around ruthenium is adequately described as distorted octahedral with the $C_5H_5$ ligand occupying three sites. The P(1)–Ru–P(2) angle (82.8°) is in the typical range for five-membered chelate rings. The two P–Ru–Cl angles (Table 1) differ by only 4.2°, much less than the corresponding angle difference in [CpRu((*S*,*S*)-CHIRAPHOS)Cl], 10.9° [17]. The bond distances around the ruthenium atom are normal, the Ru–P bonds of **6** are actually slightly shorter than those of the CHIRAPHOS complex (av. 228.3 pm). Furthermore, the P–C bond distances within the phosphole rings are also somewhat smaller than the P–C(*ipso*) distances of the CHIRAPHOS complex (av. 185.1 pm) [17] while the P–C(backbone) bonds of both compounds have exactly the same length. Both dibenzophosphole systems are perfectly flat and, somewhat surprisingly, also almost exactly coplanar (Fig. 2). The geometrical situation is thus quite different from that in [CpRu((*S*,*S*)-CHIRAPHOS)Cl] where the Cl ligand is exposed on one side to the edge and on the other side to the face of a phenyl group (Fig. 3). The configuration at the two asymmetric carbon atoms is (*S*) as indicated by the Flack parameter (0.014).

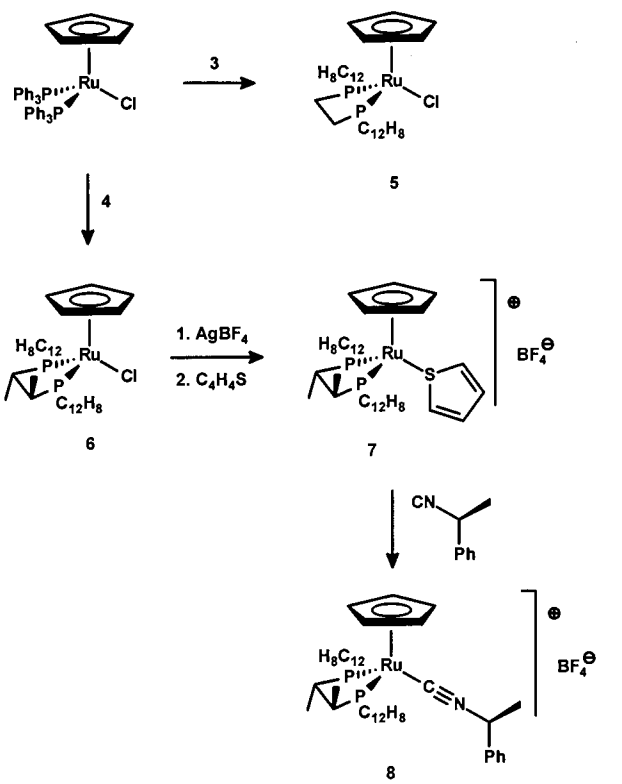
### 2.3. Ligand substitution reactions of $[CpRu(C_{12}H_8PCHMeCHMePC_2H_8)Cl]$ (6)

Compared to other chelate complexes of the type $[CpRu(Ph_2P–PPh_2)Cl]$, the compound **6** displayed a surprising lack of reactivity. Thus, while [CpRu((*S*,*S*)-CHIRAPHOS)Cl] or the achiral analog [CpRu(dppe)Cl] exchange the chloride ligand for thioethers or sulfoxides upon brief refluxing in methanol [4], we were unable to detect any reaction of **6** with amines, thioethers, or even tertiary phosphines. Complex **6**, however, did react with $AgBF_4$ and thiophene to give the thiophene complex **7** as an orange-colored, air-stable compound. This stability




Scheme 2. Reaction scheme for phenyldibenzophosphole (**1**) producing lithium dibenzophospholide (**2**), 1,2-bis(dibenzophospholyl)ethane (**3**) and (2*S*,3*S*)-bis(dibenzophospholyl)butane (**4**).

is again surprising since thiophene complexes of this type usually are highly labile and air-sensitive [18–20]. Due to residual silver salts **7** could not be completely




Scheme 3. Reaction of ligand **3** and crude **4** with $[CpRu(PPh_3)_2Cl]$ in refluxing toluene giving high yields of the orange-colored crystalline compounds **5** and **6**, respectively. Complex **6** is then further reacted with $AgBF_4/C_4H_4S$ to produce the thiophene complex **7** and with (*S*)-CNCHMePh to produce **8**.

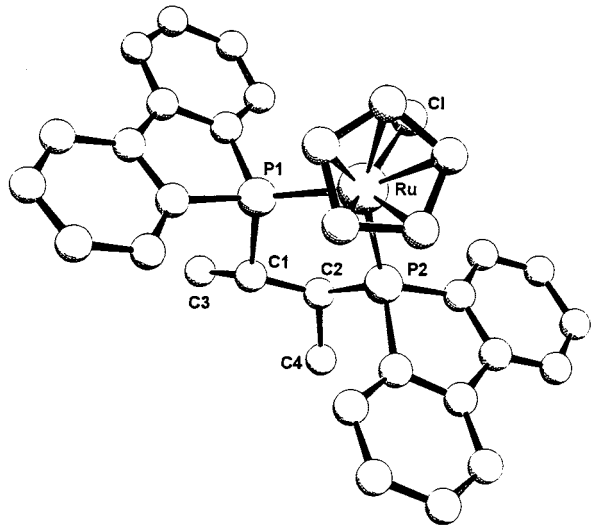



Fig. 1. Molecular structure and partial atomic numbering scheme of $[CpRu((S,S)\text{-}C_{12}H_8PCHMeCHMePC_{12}H_8)Cl]$ (**6**).

purified and was therefore characterized spectroscopically. Of note is the accidental degeneracy of the two $^{31}P$-NMR signals which coincide to a slightly broadened singlet.

Complex **7** reacted slowly with (*S*)-1-phenylethyl isocyanide to give the diastereomerically pure $[CpRu((S,S)\text{-}C_{12}H_8PCHMeCHMePC_{12}H_8)((S)\text{-}CNCHMePh)]BF_4$ (**8**) as off-white, air-stable crystalline powder. Care was taken to spectroscopically analyze the crude reaction mixture for any of the opposite diastereomer which should have been detected if present in $>2–3\%$ abundance.

## 3. Discussion

The synthesis of (2*S*,3*S*)-bis(dibenzophospholyl)butane (**4**) from readily available starting materials

Table 1
Selected bond distances (pm) and angles (°) for $[CpRu((S,S)\text{-}C_{12}H_8PCHMeCHMePC_{12}H_8)Cl]$ (**6**)

| Atoms | Bond distances (pm) | Atoms | Bond angles (°) |
|---|---|---|---|
| Ru–Cl | 244.0(1) | Cl–Ru–P(1) | 93.92(3) |
| Ru–P(1) | 225.8(1) | Cl–Ru–P(2) | 89.73(4) |
| Ru–P(2) | 225.5(1) | P(1)–Ru–P(2) | 82.80(4) |
| Ru–C(51) | 220.3(3) | Ru–P(1)–C(1) | 112.39(11) |
| Ru–C(52) | 217.7(4) | Ru–P(1)–C(11) | 119.36(11) |
| Ru–C(53) | 218.7(3) | Ru–P(1)–C(21) | 112.69(10) |
| Ru–C(54) | 221.9(4) | Ru–P(2)–C(2) | 112.36(10) |
| Ru–C(55) | 222.4(4) | Ru–P(2)–C(31) | 115.06(11) |
| Ru–Cp[a] | 185.7 | Ru–P(2)–C(41) | 123.78(10) |
| P(1)–C(1) | 186.2(3) | P(1)–C(1)–C(2) | 109.1(2) |
| P(2)–C(2) | 185.8(3) | P(2)–C(2)–C(1) | 107.9(2) |
| C(1)–C(2) | 153.0(4) | | |

[a] Cp denotes the midpoint of the $C_5H_5$ ring.

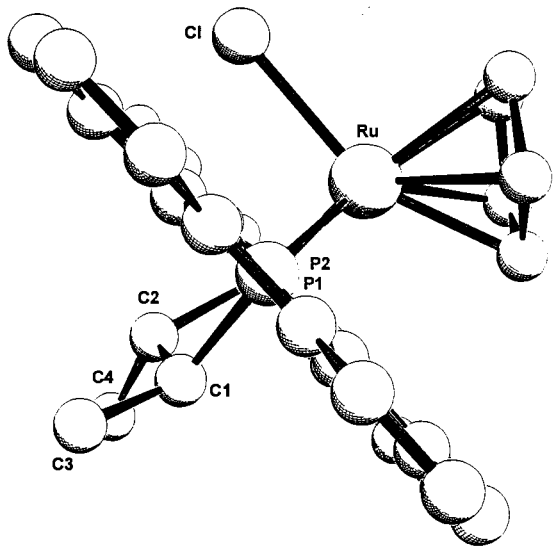



Fig. 2. Side view of **6** emphasizing the coplanarity of the two bis(dibenzophosphole) moieties. Dihedral angles: P1–C1–C2–P2 41.5(3), C3–C1–C2–C4 −63.1(4)°.

(phenyldibenzophosphole is obtained in high yield from tetraphenylphosphonium bromide [21]) is straightforward and should pose no problems with regard to scaleup. The material isolated after chromatography is pure enough to be employed for the synthesis of transition metal complexes. As a chelate ligand of the 1,2-bis(phosphino)alkane type **4** exhibits no unusual behaviour: bond angles and bond lengths in the complex **6** are perfectly within the normal range which indicates that no excessive steric strain exists within the molecule. Nevertheless, it is undoubtedly the interaction with the $C_5H_5$ ligand which forces the two dibenzoposphole moieties into a common plane (Fig. 2). From a comparison of the dihedral angles P–C–C–P and C–C–C–C within the chelate backbones of **6** and

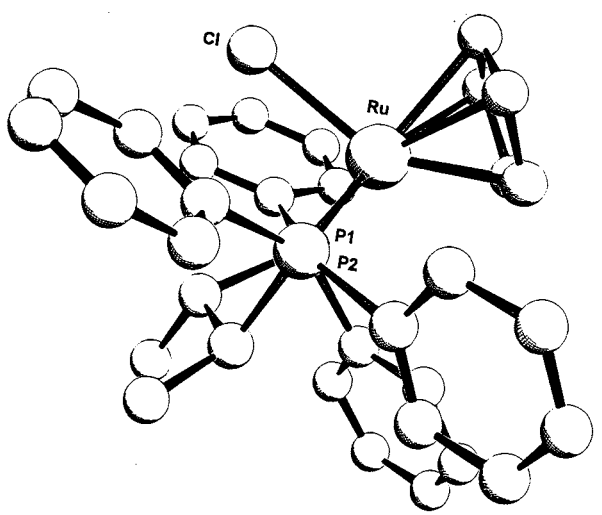



Fig. 3. Side view of [CpRu((*S*,*S*)-CHIRAPHOS)Cl]. Dihedral angles P–C–C–P 53.3, C–C–C–C −52.2°. Data taken from ref. [17].

[CpRu((*S*,*S*)-CHIRAPHOS)Cl] it is apparent that this part of the molecule can readily accommodate sizable distortions. The disappointing result, in the present context, is due to the fact that any substrate molecule introduced into **6** in place of the chloride ligand experiences an environment of almost perfect mirror symmetry. The situation should of course be different in square-planar complexes where the two dibenzophosphole moieties would be able to rotate more freely and assume a tilted orientation. We, therefore, still expect the ligand **4** to have some potential in asymmetric catalysis.

The low reactivity in ligand substitution reactions is another surprising feature in the chemistry of **6** and **7**. As Figs. 1 and 2 show it is neither a steric blocking nor other kinds of geometrical constraints that would not allow an incoming ligand to take up the site vacated by the $Cl^-$ and thiophene ligands, respectively. We therefore assume that ligand substitution in typical $[CpRu(PR_3)_2X]$ complexes including those where $(PR_3)_2$ = dppe, (*S*,*S*)-CHIRAPHOS (and probably in organophosphine-containing complexes in general) is accelerated by a mechanism which deserves more widespread consideration.

Ligand substitution reactions of $d^6$-octahedral complexes usually proceed by a dissociatively activated ($I_d$) mechanism where the rate-determining step is dominated by the rupture of the metal–ligand bond. The first intermediate is a coordinatively unsaturated complex which may be trapped either by the incoming ligand or by a solvent molecule [22–24]. In the past, a number of such 16 valence-electron species containing organophosphine ligands have been isolated and characterized crystallographically. A recurring feature is the existence of an agostic M···H–C interaction of the metal atom with one of the organic groups of the phosphine ligands [25–27].The formation of such an agostic bond lowers the energy of the transition state by

Table 2
Crystallographic data for [CpRu((*S*,*S*)-$C_{12}H_8PCHMeCHMePC_{12}H_8$)-Cl] (6)

| | |
|---|---|
| Chemical formula | $C_{33}H_{29}ClP_2Ru$ |
| Formula weight | 624.02 |
| Temperature (K) | 293 |
| Space group | $P2_1$ (no. 4) |
| *a* (pm) | 820.6(4) |
| *b* (pm) | 1501.0(3) |
| *c* (pm) | 1172.8(6) |
| $\beta$ (°) | 108.87(2) |
| *V* ($pm^3$) | $1.3671(9) \times 10^9$ |
| *Z* | 2 |
| *l* (pm) | 70.930 |
| $D_{calc.}$ (g $cm^{-1}$) | 1.516 |
| $\mu$ ($cm^{-1}$) | 1.83 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0185 |
| $wR_2$ [$I > 2\sigma(I)$][a] | 0.0487 |

[a] $wR_2 = \{[\Sigma w(F_c^2 - F_o^2)^2]/[\Sigma w(F_o^2)^2]\}^{0.5}$.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **6**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Ru | 9590(1) | 10000(1) | 9922(1) | 33(1) |
| P(1) | 8857(1) | 9195(1) | 11308(1) | 33(1) |
| P(2) | 7338(1) | 9275(1) | 8629(1) | 33(1) |
| Cl | 7695(1) | 11240(1) | 9978(1) | 47(1) |
| C(1) | 7156(4) | 8356(2) | 10609(3) | 39(1) |
| C(2) | 5971(4) | 8719(2) | 9408(3) | 37(1) |
| C(3) | 6208(5) | 8014(3) | 11446(4) | 58(1) |
| C(4) | 4757(4) | 8019(3) | 8627(3) | 51(1) |
| C(11) | 10480(4) | 8519(2) | 12378(3) | 40(1) |
| C(12) | 11472(5) | 7841(2) | 12132(4) | 51(1) |
| C(13) | 12662(5) | 7415(3) | 13091(5) | 66(1) |
| C(14) | 12840(5) | 7638(3) | 14253(4) | 67(1) |
| C(15) | 11856(5) | 8304(3) | 14507(3) | 58(1) |
| C(16) | 10651(4) | 8757(2) | 13565(3) | 43(1) |
| C(21) | 8343(4) | 9742(2) | 12532(3) | 39(1) |
| C(22) | 9476(4) | 9475(2) | 13648(3) | 44(1) |
| C(23) | 9420(5) | 9898(4) | 14700(3) | 58(1) |
| C(24) | 8231(6) | 10561(3) | 14611(4) | 67(1) |
| C(25) | 7083(6) | 10810(3) | 13507(4) | 63(1) |
| C(26) | 7120(5) | 10404(2) | 12456(3) | 49(1) |
| C(31) | 7896(4) | 8470(2) | 7665(3) | 38(1) |
| C(32) | 9103(4) | 7785(2) | 8003(3) | 46(1) |
| C(33) | 9489(5) | 7303(3) | 7116(4) | 58(1) |
| C(34) | 8707(5) | 7510(3) | 5917(4) | 61(1) |
| C(35) | 7501(5) | 8179(3) | 5573(3) | 56(1) |
| C(36) | 7079(4) | 8670(2) | 6446(3) | 43(1) |
| C(41) | 5785(4) | 9795(2) | 7335(3) | 38(1) |
| C(42) | 4659(4) | 10493(2) | 7329(4) | 52(1) |
| C(43) | 3635(5) | 10818(3) | 6231(4) | 63(1) |
| C(44) | 3726(5) | 10474(3) | 5174(4) | 66(1) |
| C(45) | 4820(5) | 9773(3) | 5169(3) | 57(1) |
| C(46) | 5870(4) | 9424(2) | 6267(3) | 43(1) |
| C(51) | 12390(4) | 9952(5) | 10852(4) | 70(1) |
| C(52) | 11954(5) | 9359(3) | 9889(5) | 65(1) |
| C(53) | 11312(5) | 9868(4) | 8845(4) | 70(1) |
| C(54) | 11303(5) | 10757(3) | 9146(5) | 69(1) |
| C(55) | 11990(5) | 10808(3) | 10410(5) | 70(1) |

$U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

more than 10 kJ $mol^{-1}$ and thus accelerates ligand dissociation [28]. The dibenzophosphole substituents of **5–7** obviously cannot provide such an internal M···H–C stabilization which in turn explains their low reactivity. Thus it seems that dibenzophosphole ligands such as **3** or **4** are even better suited than the traditional bis(diphenylphosphino)alkanes for the purpose of stabilizing low-valent transition metal complexes.

## 4. Experimental section

All manipulations were carried out in Schlenk-type glassware under an atmosphere of purified nitrogen or argon. Solvents were dried and distilled under nitrogen prior to use. NMR solvents were degassed and stored under nitrogen over molecular sieves. NMR: Bruker AMX 400; chemical shifts are reported in ppm versus TMS ($^1H$, $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$).

The following starting materials were prepared by published procedures: Phenyldibenzophosphole [21], [$CpRu(PPh_3)_2Cl$] [29], (*S*)-1-phenylethyl isocyanide [30]. All other reagents were used as obtained commercially.

### 4.1. 1,2-Bis(dibenzophospholyl)ethane (3)

To a solution of phenyldibenzophosphole (**1**) (4.00 g, 15.4 mmol) in THF (70 ml) freshly cut lithium (2.00 g, 0.29 mol) was added. The mixture was stirred 2 h at r.t. and then immersed into an ultrasonic cleaning bath for 2 h. *t*-Butylchloride (1.67 ml, 15.4 mmol) was added to quench phenyllithium, and after addition of ethyleneglycol ditosylate (2.85 g, 7.70 mmol) the mixture was stirred for another 6 h at r.t. After evaporation to dryness the mixture was redissolved in toluene (50 ml) and 2 M HCl (50 ml). The organic phase was separated, washed with water, and evaporated to dryness. The residue was redissolved in dichloromethane and flash chromatographed over a short silica column. Recrystallization from 2-propanol gave pure **3** as colorless crystalline material. Yield 2.24 g (74%), m.p. 185°C (lit. 187°C). $^1H$-NMR (400 MHz, $CDCl_3$): $\delta$ 1.49 (vt, $J$ = 11.8 Hz, $C_2H_4$), 7.29, 7.43, 7.88 (m, aryl). $^{31}P$-NMR (162 MHz, $CDCl_3$): $\delta$ −10.8 (s). Anal. Calc. for $C_{26}H_{20}P_2$ (394.4): C 79.18, H 5.11. Found: C 78.61, H 5.32%.

### 4.2. (2S,3S)-Bis(dibenzophospholyl)butane (4)

A solution of lithium dibenzophospholide (**2**) was prepared and treated with (2*R*,3*R*)-butanediol ditosylate (3.07 g, 7.70 mmol) as described above. After evaporation to dryness the oily residue was taken up in a 1:1 mixture of ethanol and ether (100 ml), filtered, evaporated, and flash chromatographed over a short silica column using cyclohexane as an eluent. After evaporation of the solvent and prolonged drying under vacuum a colorless semisolid product remained. Yield 2.93 g (90%). $^1H$-NMR (400 MHz, $CDCl_3$): $\delta$ 0.75 (m, $CH_3$), 1.93 (m, CH), 6.70–7.60 (m, aryl). $^{31}P$-NMR (162 MHz, $CDCl_3$): $\delta$ −4.3 (s).

### 4.3. [CpRu($C_{12}H_8PC_2H_4PC_{12}H_8$)Cl] (5)

A solution of [$CpRu(PPh_3)_2Cl$] (1.45 g, 2.00 mmol) and **3** (0.80 g, 2.03 mmol) in toluene (60 ml) was heated under reflux for 5 h. The mixture was then taken to dryness, the residue dissolved in dichloromethane (7 ml), and the product precipitated by adding pentane (30 ml). The raw material was placed on a silica column, triphenylphosphine was eluted with toluene and the product removed from the column with a 1:1 mixture of acetone/dichloromethane. Recrystallization from

dichloromethane/pentane gave the pure compound. Yield 1.05 g (88%), orange crystalline powder, m.p. 110°C (dec.). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 1.92, 2.21 (m, $C_2H_4$), 4.39 (s, $C_5H_5$), 7.35–7.55, 7.90–8.00 (m, aryl). $^{31}$P-NMR (162 MHz, $CDCl_3$): $\delta$ 70.4 (s). Anal. Calc. for $C_{31}H_{25}ClP_2Ru$ (596.0): C 62.47, H 4.23. Found: C 62.38, H 4.31%.

### 4.4. [CpRu((S,S)-$C_{12}H_8$PCHMeCHMePC$_{12}H_8$)Cl] (6)

This compound was prepared as described above for **5**. Yield 1.06 g (85%), orange crystalline powder. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.39 (dd, $^3J$(P,H) = 12.1 Hz, $^3J$(H,H) = 6.8 Hz, $CH_3$), 0.45 (dd, $^3J$(P,H) = 12.4 Hz, $^3J$(H,H) = 6.8 Hz, $CH_3$), 1.80, 2.33 (m, CH), 4.36 (s, $C_5H_5$), 7.30–7.60, 7.95, 8.35, 8.70 (m, aryl). $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 12.2 (dd, $^2J$(P,C) = 17 Hz, $^3J$(P,C) = 5 Hz, $CH_3$), 13.7 (dd, $^2J$(P,C) = 18 Hz, $^3J$(P,C) = 4 Hz, $CH_3$), 41.9 (dd, $^1J$(P,C) = 27 Hz, $^2J$(P,C) = 19 Hz, CH), 43.2 (dd, $^1J$(P,C) = 27 Hz, $^2J$(P,C) = 20 Hz, CH), 80.0 (s, $C_5H_5$), 120–144 (m, aryl). $^{31}$P-NMR (162 MHz, $CDCl_3$): $\delta$ 72.6 (d, $^2J$(P,P) = 43 Hz), 75.4 (d, $^2J$(P,P) = 43 Hz). Anal. Calc. for $C_{33}H_{29}ClP_2Ru$ (621.1): C 63.51, H 4.68. Found: C 62.80, H 4.86%.

### 4.5. [CpRu((S,S)-$C_{12}H_8$PCHMeCHMePC$_{12}H_8$)-($SC_4H_4$)]$BF_4$ (7)

To a solution of **6** (0.12 g, 0.19 mmol) and thiophene (0.10 ml, 1.25 mmol) in dichloromethane (10 ml) $AgBF_4$ (50 mg, 0.26 mmol) was added at 0°C. After 1 h the mixture was filtered over Celite and the product precipitated by adding ether (10 ml). Yield 0.12 g (86%), orange microcrystalline powder. $^1$H-NMR (400 MHz, $CD_2Cl_2$): $\delta$ 0.62 (m, $CH_3$), 2.17 (m, CH), 4.27 (s, $C_5H_5$), 6.64, 6.99 (m, $SC4H_4$), 7.40–8.20 (m, aryl). $^{31}$P-NMR (162 MHz, $CDCl_3$): $\delta$ 75.3 (br).

### 4.6. [CpRu((S,S)-$C_{12}H_8$PCHMeCHMePC$_{12}H_8$)((S)-CNCHMePh)]$BF_4$ (8)

To a solution of **7** (50 mg, 68 μmol) in dichloromethane (5 ml) was added (*S*)-CNCHMePh (50 mg, 0.38 mmol). After 1 h the mixture was filtered over Celite, the filtrate evaporated to 1 ml, and the product precipitated by adding hexane. Yield 40 mg (73%), off-white microcrystalline powder. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.44 (m, $CH_3$), 1.65 (d, $^3J$(H,H) = 6.7 Hz, $CH_3$), 1.95, 2.06 (m, CH), 4.69 (s, $C_5H_5$), 5.54 (q, $^3J$(H,H) = 6.7 Hz, CH), 7.30–8.00 (m, aryl). $^{31}$P-NMR (162 MHz, $CDCl_3$): $\delta$ 75.2 (d, $^2J$(P,P) = 35 Hz), 79.3 (d, $^2J$(P,P) = 35 Hz). Anal. Calc. For $C_{42}H_{38}BF_4NP_2Ru$ (806.6): C 62.54, H 4.75, N 1.74. Found: C 62.21, H 4.66, N 1.57%.

### 4.7. X-ray structure determination of [CpRu((S,S)-$C_{12}H_8$PCHMeCHMePC$_{12}H_8$)Cl] (6)

Clear orange crystals of **6** were obtained from dichloromethane/hexane. Twenty-five centered reflections from a crystal of the size $0.50 \times 0.50 \times 0.30$ mm$^3$ in the range $10 < \theta < 14°$ gave a monoclinic unit cell of the dimensions listed in Table 2. Data were collected from one-fourth of the reflection sphere in the range $2 < \theta < 27°$ (Enraf-Nonius CAD diffractometer, Mo–$K_\alpha$ radiation, graphite monochromator, filter factor 15.41). An empirical absorption correction based on the intensities of nine reflections was applied. The structure was solved by the Patterson method in the space group $P2_1$ (no.4) using the SHELXS86 [31] program package. Hydrogen atoms were included in fixed positions, coupled to their respective C atoms. Least-squares cycles using the SHELXL93 [32] program package led to the *R* values given in Table 2. Atomic coordinates are listed in Table 3. The configuration at the two asymmetric C atoms was verified by a Flack parameter of 0.014. Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-408034.

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