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Preliminary Communication

Chiral phosphine complexes of ruthenium(II) arenes *

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Abstract

Chiral, arene-containing complexes of ruthenium(II) based on the phosphines chiraphos and diop are reported, as well as improved routes to some known analogues containing binap or the achiral phosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2$, dppe; $n = 4$, dppb).

The recently reported [1] use of $\text{RuCl}(\text{C}_6\text{H}_6)(\text{CH}_3\text{-CN})_2^+\text{PF}_6^-$ as a precursor to the cationic species $\text{RuCl}(\text{C}_6\text{H}_6)(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{PPh}_2)^+\text{PF}_6^-$ prompts us to describe our work on the preparation by this route of analogous arene complexes containing chiral chelating phosphines. Arene complexes of Ru^{II} have shown promising results in catalytic hydrogenation of olefins [2–4], ketones [3,5], and arenes [4,6], and have met with some success in the ring-opening metathesis polymerization of cycloolefins [7]. Cationic, arene complexes containing one chelating chiral phosphine per metal are particularly effective for catalytic asymmetric hydrogenation, but only one such class of compounds has been isolated, the binap derivatives initially reported in 1989 [3]. We now describe preparation of $\text{RuCl}(\text{C}_6\text{H}_6)(\text{PP})^+\text{PF}_6^-$ and $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2(\mu\text{-PP})$ (where PP = chiraphos, diop), as well as development of more facile routes to some known complexes of binap and the achiral phosphines dppb and dppe [8–10].

Existing routes to the cationic complexes [3,8], typically based on the halide-bridged dimer $[\text{RuCl}(\text{C}_6\text{H}_6)]_2(\mu\text{-Cl})_2$ **1** as a starting material [11], are hampered by side-reactions for all but rather bulky or rigid diphosphines (such as binap or, as recent work suggests [12], the dicyclohexylphosphine $\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2$). Inade-

quate stoichiometric control results in contamination of the desired products (containing a single diphosphine per ruthenium) by the phosphine-bridged species $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2(\mu\text{-PP})$, as well as mononuclear bis(PP) species formed by loss of arene (Table 1). Side-reactions are promoted by the initially poor solubility in ethanol of both **1** (which, if prepared by the original method [13,14], we and others [11,15] find to be an insoluble oligomer rather than a dimer) and the phosphine, and the elevated temperatures required. Selectivity problems appear to be a function of the size of the ring formed on chelation of the diphosphine, and increase with decreasing steric bulk; these are particularly severe for diphosphines forming a five-membered chelate ring, presumably due to the high thermodynamic stability of this configuration. On treatment of oligomeric **1** (possibly $[\text{RuCl}_2]_n[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2$) with dppe or chiraphos in refluxing ethanol, *trans*- $\text{RuCl}_2(\text{PP})_2$ is obtained as the principal product. Even with dimeric **1**, side-reactions arising from arene displacement and formation of bridged species remain of concern, the byproducts accounting for the bulk of the starting phosphine. Dppb and diop, which like binap form seven-membered chelate rings, have a reduced tendency to form bis(diphosphine) species. These ligands cannot in fact generate the corresponding *trans*- $\text{RuCl}_2(\text{PP})_2$ complexes [16,17], presumably owing to steric limitations (although related species in which one of the *trans* groups is of lower steric bulk have been reported, e.g. *trans*- $\text{RuHCl}(\text{dppb})_2$ [18], $\text{RuH}(\text{H}_2)(\text{binap})_2^+\text{PF}_6^-$ [19]). Phosphine-bridged byproducts may be formed more readily, depending on the flexibility of the phosphine backbone. Thus reaction of oligomeric **1** with dppb or diop gives a mixture of the desired cationic and the phosphine-bridged products, while with binap only the cationic species (and unreacted starting materials) is obtained. Dimeric **1** gives with diop or binap solely $\text{RuCl}(\text{C}_6\text{H}_6)(\text{PP})^+\text{Cl}^-$, but from 15 to 25% of the less rigid phosphine dppb is lost as $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2(\mu\text{-dppb})$. As the variable product selectivity can be regarded as a consequence of carrying out the bridge-cleavage and subsequent phosphine-substitution reactions in a one-pot procedure, we sought to alleviate the problem by use of a mononuclear starting material with high solubility in organic solvents. Four species, all accessible in high yield from **1**, were investigated: $\text{RuCl}_2(\text{C}_6\text{H}_6)\text{L}$; L = CH_3CH_2

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* Dedicated to Professor Michael F. Lappert on the occasion of his 65th birthday.

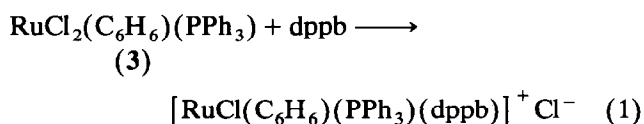
TABLE 1. ³¹P{¹H} NMR data for chelating and bridging phosphine complexes ^a

Phosphine	RuCl(C ₆ H ₆)(PP) ⁺ Cl ⁻	[RuCl ₂ (C ₆ H ₆) ₂ (μ-PP)]	trans-RuCl ₂ (PP) ₂
dppe	70.4 (s) ^b	23.3 (s) ^b	45.0 (s) ^b
dppb	30.5 (s) ^b	25.0 (s) ^b	-
chiraphos	66.0, 71.8 (ABq, J = 44) ^b	31.5 (m), 34.8 (m) ^{c,d}	47.1 (s) ^b
diop	23.9, 25.8 (ABq, J = 57) ^b	22.3 (s) ^c	-
binap	30.1, 37.9 (ABq, J = 64) ^b	-	-

^a 121 MHz, CDCl₃, 85% H₃PO₄ external standard; s = singlet, ABq = AB quartet, J in Hz. ^b The complex has been isolated (sometimes as the PF₆⁻ salt) and gives satisfactory elemental analysis. ^c *In situ* species, characterized by ³¹P{¹H} and ¹H NMR. ^d Resolved at -50°C; δ 31.4, 34.8 (ABq, J = 58).

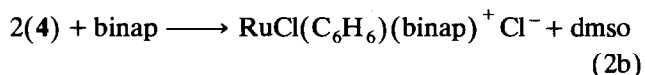
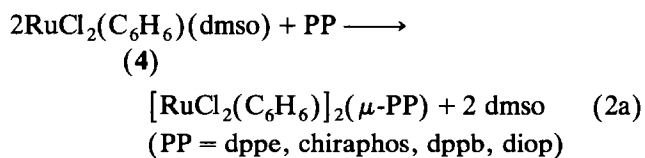
[20*], PPh₃ **3** [14], dmsO **4** [21], and RuCl(C₆H₆)-(CH₃CN)₂⁺PF₆⁻ **5** (use of which in this context was reported [1] during the course of this work). Of these, the mono-acetonitrile species **2** was ruled out immediately on the basis of its low solubility. The remaining three complexes were screened in model studies with dppb and dppe before reactions with the chiral phosphines were undertaken.

The PPh₃ derivative **3** reacts slowly with dppb at room temperature. Only 20% free triphenylphosphine is evident in the *in situ* ³¹P{¹H} NMR spectrum over 24 h in CDCl₃, and the expected singlet at δ 30.5 for RuCl(C₆H₆)(dppb)⁺Cl⁻ **6** (Table 1) is not observed. Refluxing for up to 4 h in CH₂Cl₂-methanol gives a small amount of **6**, but the principal product is a mixed phosphine species, possibly RuCl(C₆H₆)(PPh₃)-(dppb)⁺Cl⁻, in which the diphosphine is monodentate [22*] eqn. (1). Longer reaction times led to side-reactions with little increase in the amount of the desired **6**. As the PPh₃ ligand was not readily replaced, use of **3** was not further investigated.



On treatment with dppb in refluxing CH₂Cl₂-methanol, the dmsO complex **4** gives **6** as the principal product, contaminated however by 10% of the bridged complex [RuCl₂(C₆H₆)₂(μ-dppb)] **7**, as well as varying amounts of disubstituted material. Lowering the reaction temperature resulted in exclusive formation of **7**, suggesting that the cationic complex **6** is formed by reaction of residual phosphine with the bridged species, rather than by direct reaction with **4**. Isolation of **6** via reaction of **7** with dppb in refluxing ethanol was previously described [8]. The appearance of some bis(dppb) material implies that the cationic species is either less thermally stable than the bridged, or that (owing to the

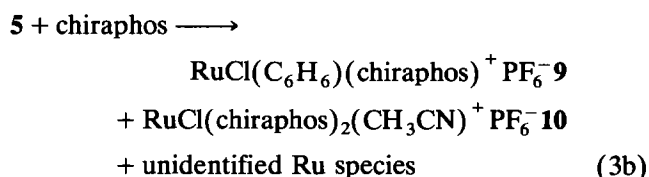
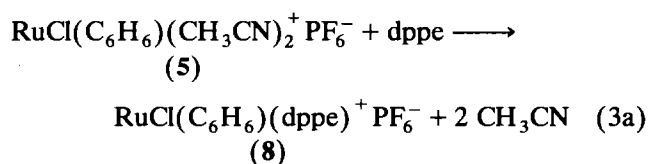
extreme insolubility of the latter) phosphine attacks **6** before reaction with **7** is complete. In either case a mixture of products is unavoidable. Similarly, reaction of **4** with one equivalent of dppe gives a mixture of the bridged, chelated cation, and bis(dppe) products at room temperature; at reflux trans-RuCl₂(dppe)₂ is obtained as the only phosphine-containing product. Of interest, the dmsO complex proves an excellent precursor to the phosphine-bridged species; such complexes of dppe, chiraphos, dppb and diop can be prepared cleanly, instantaneously, and in quantitative yield by addition of half an equivalent of diphosphine to **4** in CH₂Cl₂ at room temperature (eqn. (2a)). The μ-dppe and -dppb complexes were previously prepared by reaction of **1** with phosphine in refluxing benzene [8]. Binap, owing to its bulk and rigidity, does not form the corresponding bridged species, giving under these conditions RuCl(C₆H₆)(binap)⁺Cl⁻ and unreacted starting material (eqn. (2b)). Use of one equivalent of binap furnishes solely the cationic complex, in a much more facile synthesis of this useful catalyst than that originally reported [3].



The less labile bis(nitrile) species **5** gives several side-products in addition to **6** on reaction with one equivalent of dppb in acetonitrile at room temperature. An intermediate species containing monodentate dppb, probably RuCl(C₆H₆)(MeCN)(dppb)⁺PF₆⁻ as judged by ³¹P{¹H} NMR data (two singlets; δ 28.4, -18.1), slowly gives way to **6**, accompanied however by an approximately equal amount of disubstituted material. With dppe, on the other hand, RuCl(C₆H₆)(dppe)⁺PF₆⁻ **8** is formed as the principal product (eqn. (3a)). No bis(dppe) byproduct is observed, even in the presence of excess phosphine. The reaction of **5** with chi-

* Reference number with asterisk indicates a note in the list of references.

raphos was therefore investigated. At room temperature, over 15 h in acetonitrile, the desired RuCl(C₆H₆)(chiraphos)⁺PF₆⁻ **9** and the bis(chelate) complex *trans*-RuCl(MeCN)(chiraphos)₂⁺PF₆⁻ **10** [23*] form in a ratio of 2:1 (eqn. (3b)). Separation is effected by washing with benzene, in which **10** is preferentially soluble. Formation of **10** in ca. 30% yield under conditions which gave no observable amount of the corresponding dppe species suggests that the driving force for formation of bis(chiraphos) complexes is considerably greater than that for the dppe analogues, and accounts for the inability to generate significant amounts of the desired product **9** under the more forcing conditions used with **1** as a precursor.



Thus use of RuCl(C₆H₆)(CH₃CN)₂⁺PF₆⁻ as a mononuclear starting material permits improved product selectivity in preparation of the cationic complexes of dppe and chiraphos, due in part to greater control over the reaction stoichiometry, and in part to obviation of the need for elevated temperatures, which promote arene loss. With dppb or diop, in contrast, the original approach is preferable; with dppb in particular, the high temperatures as used with precursor **1** may assist in conversion of the readily formed bridged byproduct to the mono-chelate complex. Where formation of the bridged species is blocked, however, as in the case of binap, the highly labile species RuCl₂(C₆H₆)(dmsO) provides an excellent precursor to the cationic product. These distinctions follow a pattern long recognized in diphosphine reaction chemistry [16,17,24], in which phosphines with a two-carbon backbone have a high propensity for formation of bis(chelates), while those possessing a four-carbon backbone have an enhanced tendency toward phosphine-bridging modes (providing the backbone is sufficiently flexible).

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- 22 ³¹P{¹H} NMR data (CDCl₃): δ 24.5, 19.9 (ABq, J = 54), -16.4(s).
- 23 Complex **10** was isolated and characterized by ³¹P{¹H} and ¹H NMR (CDCl₃): δ_P 44.1, 52.0 (A₂B₂ pattern, J = 24); δ_H 6.8–8.0 (m, 40H, Ph), 3.0 (m, 2H, CH), 2.5 (m, 2H, CH), 1.0 (s, 3H, CH₃), 0.8 (dd, 6H, CH₃), 2.5 (dd, 6H, CH₃) [m = multiplet, dd = doublet of doublets].
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