Facile complexation of 1,1'-bis(diphenylphosphino)ruthenocene (dppr) to ruthenium(II) — simple entry to stable bimetallic ruthenoruthenocenyl system

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Abstract

Phosphine exchange occurs rapidly between $RuCl_2(PPh_3)_n$ ($n = 3$, 4) and $Ru(C_5H_4PPh_2)_2$ (dppr) at room temperature to give $RuCl_2(dppr)(PPh_3)$, 1. Triphenylphosphine is more substitutionally labile than dppr in 1; selective phosphine substitution of 1 with CO and CH_3CN gives $[RuCl_2(CO)(dppr)]$ and two geometric isomers of $[RuCl_2(NCCH_3)_2(dppr)]$ respectively.

Keywords: Ruthenium; Heterobimetallics; Phosphine; Ruthenecene; Group 8; Carbonyl

1. Introduction

Metallocenyl phosphines are valuable organometallic materials with a rich chemistry [1], and are widely applied in electroactive materials [2], polymers [3] and catalysis [4]. Among the phosphines reported, 1,1'-bis(diphenylphosphino)ferrocene (dppf) is the best established in its ligand- [5] and materials-chemistry [6]. Major advantages of the choice of dppf include its tunable coordination modes, good affinity towards a variety of metals and geometric adaptability due to the multi-dimensional motional freedom inherent in the ferrocenyl moiety [7]. Many complexes containing dppf have hence been reported to have higher catalytic activities than their conventional monophosphine (e.g. PPh_3) counterparts [8]. If these benefits can be extrapolated, the catalytic potential of the ruthenium analogue, 1,1'-bis(diphenylphosphino)ruthenocene (dppr) is worth investigation in view of the following: (i) a larger separation between the C_5 rings in dppr would facilitate reductive elimination, which is the rate-determining step in many catalytic mechanisms; (ii) the bigger bite size

of dppr offers a better protection, and hence stabilization, to the unsaturated catalytic intermediates; (iii) the larger chelate angle associated with dppr promotes ring opening via phosphine dissociation. (A stable chelate ring tends to stabilize the catalytic complex but it also slows down the reductive elimination step. A chelate with a dissociable phosphine is not necessarily a disadvantage, especially if partial dissociation occurs to give a unidentate-coordinated diphosphine, since it would behave more like a monophosphine (but with the added chelation effect). The advantage of a monophosphine complex over a diphosphine complex has been attributed to the key r.d.s. which requires phosphine dissociation prior to reductive elimination. See Ref. [9].) Our recent work on Grignard cross-coupling supports these ideas. (The catalytic efficiency of $PdCl_2(dppr)$ in the Grignard coupling of PhMgBr with 1,2-dibromobenzene, which gives 2-bromobiphenyl (79%) and *o*-terphenyl (15%) in thf reflux conditions, is superior to that shown by $PdCl_2(dppf)$ and $Pd(dppf)_2$. See Ref. [10].)

Despite these apparent benefits, surprisingly, there are very few dppr complexes reported in the literature [11–14]. Among them, only a selected few are suitable models for catalytic investigations [13,14]. There is also no report on any general synthetic precursor for dppr

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complexes. In this paper, we report a facile synthetic route to dppr complexes based on $RuCl_2(PPh_3)_3$, which is probably the most important precursor to many Ru catalysts known to date [15,16]. This method also opens up a simple entry to a Ru^{II}–Ru^{II} system with a metalloruthenocenyl phosphine ring. Using phosphine substitution as a model, we would show that different ligands such as CO and CH_3CN can be introduced. The resultant dppr chelating complexes do not appear to be as labile as those reported and thus fuel further interest for them to be explored catalytically.

2. Results and discussion

$RuCl_2(PPh_3)_3$ [16] reacts with dppr [12–14] in 1:1 molar ratio at room temperature to give $RuCl_2(dppr)(PPh_3)$, 1 (see Section 3.1).

1
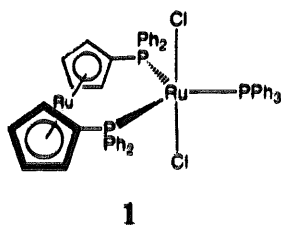
Similar reactions with other diphosphines have resulted in the isolation of $RuCl_2(dppb)(PPh_3)$ (dppb = $Ph_2P(CH_2)_4PPh_2$) but not those diphosphines with shorter methylene chains [17]. The stability of 1 is explained, as in the dppb complex, based on the large chelate bite angle of dppr. The use of $RuCl_2(PPh_3)_4$ [16], results in the same product. There is no evidence for further substitution by dppr under ambient conditions. The ¹H NMR spectrum points to an equimolar presence of dppr:PPh₃ based on the intensity ratio of the C₅ and phenyl protons. The ³¹P{¹H} NMR spectrum of 1 shows a doublet at δ −8.9 and triplet at δ 62.2 ppm at an intensity ratio of 2:1. The magnitude of $J(P,P)$ coupling (28 Hz) suggests that the ruthenocenyl phosphine and PPh_3, lie on the equatorial plane in a trigonal bipyramidal geometry, with chlorides taking up the axial sites. Surprisingly, a similar reaction of $RuCl_2(PPh_3)_3$ with dppf fails to give a product analogous to 1 (a larger bite size (and bite angle) of dppr compared with dppf may be a critical factor in the stabilization of a 16-electron unsaturated complex).

Complex 1 undergoes rapid and selective replacement of PPh₃ by CO under an atmospheric pressure of

CO gas at room temperature to give $RuCl_2(CO)(dppr)$, 2 (see Section 3.2).

2
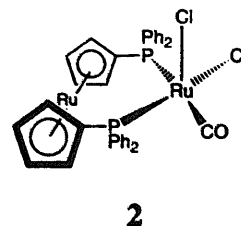
The kinetic stability of the dppr chelate is notable. In contrast to 1, complex 2 is air-stable. The IR spectrum gives a single absorption band at $1937 cm^{-1}$. This is in contrast to $RuCl_2(CO)(PPh_3)_2$ which was reported [18] to show two IR bands at 1980 and $1940 cm^{-1}$ corresponding to two geometric isomers. The ¹H NMR spectrum shows the typical resonances associated with the C₅ and phenyl ring protons and no evidence for PPh₃. The ³¹P{¹H} NMR spectrum gives two mutually-coupled doublets (δ 42.7 and 51.4 ppm) at 1:1 intensity ratio associated with the two inequivalent phosphine groups. These suggest a penta-coordinated Ru(II) with the two phosphine groups differentiated by their *trans* ligands, i.e. CO and Cl. There is no evidence that further CO addition can occur at room temperature

A mixture of 1 and CH_3CN in acetone, upon heating, readily gives $RuCl_2(NCCH_3)_2(dppr)$, 3 (see Section 3.3).

(A) *trans*   (B) *cis*

3
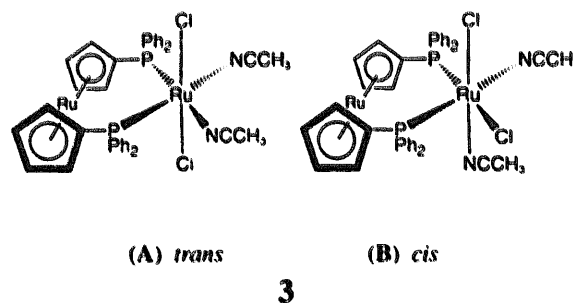
The ease of complete elimination of PPh₃, facile entry of CH_3CN and maintenance of the dppr chelate under thermal conditions are unusual features. The ³¹P{¹H} NMR spectrum of 3 reveals two geometric isomers. Isomer A corresponds to a *trans* complex with two CH_3CN groups coplanar with dppr and two mutually *trans*-chlorides completing an octahedral core. Isomer B is a *cis* complex with both chlorides and CH_3CN *cis* to each other, thereby giving two inequivalent phosphines (δ 46.3 and 56.1 ppm). The analogous

$RuCl_2(NCCH_3)_2(PPh_3)_2$ also exists as two isomers which are prepared in different solvents [19]. In solution, isomer A gradually converts to isomer B under air or argon. The higher *trans* effect of phosphines and CH_3CN probably explains the higher stability of the *cis* isomer.

In summary, the convenient and high-yield synthesis of **1** enables a facile entry to a series of Ru(II) dppr complexes. The easy replacement of PPh_3 by labile and small molecules like CH_3CN and CO not only provides a general path to a variety of dppr complexes, it further reiterates the catalytic potential of these species for activation of small molecules. The kinetic stability of dppr is suprising. The possibility for a $Ru \rightarrow Ru$ donor–acceptor bond in these species is being investigated.

3. Experimental section

3.1. $RuCl_2(dppr)(PPh_3)$, 1

To a mixture of $RuCl_2(PPh_3)_3$ (0.102 g, 0.106 mmol) and dppr (0.075 g, 0.125 mmol) was added CH_2Cl_2 (20 ml) with stirring. The colour changed from brown to dark green immediately. The resultant mixture was stirred at room temperature for 0.5 h. Vacuum evaporation followed by crystallization from CH_2Cl_2–hexane yielded dark green crystalline needles of $RuCl_2(PPh_3)(dppr) \cdot 2/3CH_2Cl_2$ (1) (0.093 g, 80%). Anal. Found: C, 57.35; H, 4.24; Cl, 11.03; P, 8.17. $C_{62}H_{43}Cl_2P_3Ru_2 \cdot 2/3CH_2Cl_2$. Calc.: C, 57.95; H, 4.06; Cl, 10.85; P, 8.53%. ^{1}H NMR (CDCl$_3$): δ 4.12 (m, 4H, C_5H_4), 5.02 (m, 4H, C_5H_4), 6.83–7.64 (m, 35H, C_6H_5) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ −8.9 (d, J(P,P) = 28 Hz, 2P, dppr), 62.2 (t, J(P,P) = 28 Hz, 1P, PPh$_3$) ppm. The product is air-sensitive and turns readily from dark green to brown upon exposure to air in CH_2Cl_2. The presence of CH_2Cl_2 solvate was confirmed in the ^{1}H NMR spectrum. Both dppf and dppr complexes are well-known to show solvates in their crystal structures. See for example Refs. [7,20].

3.2. $RuCl_2(CO)(dppr)$, 2

$RuCl_2(PPh_3)(dppr)$ (0.150 g, 0.145 mmol) was dissolved under argon in CH_2Cl_2 (15 ml). Upon flushing with CO gas, the solution instantaneously turned brown. Vacuum evaporation followed by crystallization from CH_2Cl_2–hexane yielded brown-yellow crystals of $RuCl_2(CO)(dppr)$ (2) (0.087 g, 75%). Anal. Found: C, 52.54; H, 3.76; Cl, 8.94; P, 8.49. $C_{35}H_{28}Cl_2OP_2Ru_2$. Calc.: C, 52.56; H, 3.50; Cl, 8.89; P, 7.76%. IR (KBr): ν(CO) 1937 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.90 (m, 4H, C_5H_4), 5.08 (m, 4H, C_5H_4), 7.25–7.84 (m, 20H, C_6H_5)

ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 42.7 (d, J(P,P) = 23 Hz, 1P, dppr), 51.4 (d, J(P,P) = 23 Hz, 1P, dppr) ppm.

3.3. $RuCl_2(NCCH_3)_2(dppr)$, 3

To $RuCl_2(PPh_3)(dppr)$ (0.150 g, 0.145 mmol) in acetone (40 ml) was added CH_3CN (15 ml) and the solution was heated under reflux for 2 h to give a yellow suspension. Upon concentration and filtration, the crude solid was crystallized from CH_2Cl_2–acetone–hexane to yield $RuCl_2(NCCH_3)_2(dppr)$ (3) as brown-yellow crystals (0.076 g, 61%). Anal. Found: C, 53.24; H, 3.90; Cl, 10.13; N, 3.19; P, 7.23. $C_{38}H_{34}Cl_2N_2P_2Ru_2 \cdot$ 1/4CH$_2$Cl$_2$. Calc.: C, 52.50; H, 3.95; Cl, 10.15; N, 3.20; P, 7.09%.

(a) Under argon in CDCl$_3$ after 1 h. ^{1}H NMR (CDCl$_3$): δ 1.58 (s, *cis*-CH$_3$), 1.72 (s, 6H, *trans*-CH$_3$), 2.00 (s, *cis*-CH$_3$), 4.75 (m, 4H, C_5H_4), 4.94 (m, 4H, C_5H_4), 7.17–8.12 (m, 20H, C_6H_5) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 40.3(s), 46.3 (d, J(P,P) = 29 Hz), 56.1 (d, J(P,P) = 29 Hz) ppm.

(b) Under argon in CDCl$_3$ overnight. ^{1}H NMR (CDCl$_3$): δ 1.59 (s, 3H, CH$_3$), 2.00 (s, 3H, CH$_3$), 4.50 (m, 4H, C_5H_4), 4.84 (m, 4H, C_5H_4), 7.11–7.50 (m, 20H, C_6H_5) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 46.4 (d, J(P,P) = 29 Hz), 56.3 (d, J(P,P) = 29 Hz) ppm.

(c) In the presence of air overnight in CDCl$_3$. The NMR data are the same as (b).

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