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A Simple General Route to Chelate Diphosphine Ruthenium (II) Complexes.

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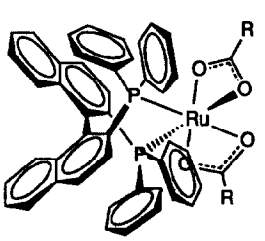
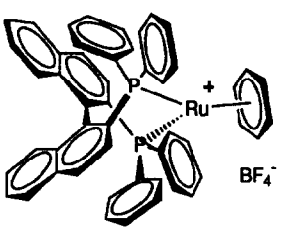
Summary Displacement of cyclooctadiene from its ruthenium 2-propenyl hexafluoropentanedionate complex by diphosphines affords the corresponding chelate diphosphine complexes, which are precursors to active hydrogenation catalysts.

The high enantioselectivity and broad applicability of ruthenium BINAP complexes for homogeneous hydrogenation will ensure their continuing importance in asymmetric synthesis[1]. In practice, the catalyst is introduced as the ruthenium (II) bis-acetate (**1a**) or bis-trifluoroacetate (**1b**), a related dihalide complex or the cationic arene complexes of structure (**2**). The synthesis of (**1a**) and (**1b**) involves a two-step procedure in which the ligand is introduced at the outset[2]; other chelating phosphines give diverse products. The dihalide complexes are prepared directly from (**1a**)[3]. Cationic complexes of type (**2**) are prepared by the reaction of the biphosphine with the appropriate areneruthenium dihalide[4]. The complexes (**3a**) and (**3b**) which are closely related to (**1a**) and (**1b**) have been prepared simply[5] and in high yield from reactants related to the bridged binuclear Ru carboxylate complexes described by Singleton and co-workers[6].



1 a R=CH_3
b R=CF_3



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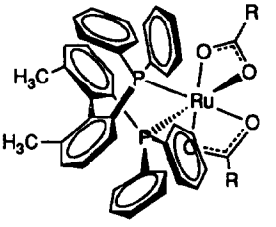

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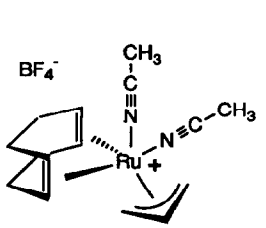
(S-enantiomers drawn)

During the course of a project designed to extend the understanding and range of ruthenium asymmetric hydrogenation, we wished to develop a method for the synthesis of diphosphine complexes with specific constraints. Thus the method should be applicable to any chelating diphosphine, which should preferably be introduced in the last step. The complex should be of the form P_2RuXY, where the groups X and Y can be

activated and removed differentially, so as to provide opportunities for characterisation of reactive intermediates under catalytic conditions.

Some years ago Lewis and co-workers reported the synthesis of cyclooctadiene complex (**4**) and its reaction with Tl (acac) to form (**5a**)[7]. Complex (**4**) was reported to react with bipyridyl or o-phenylenebis-(dimethyl arsine) to afford the products of replacement of the diene, but the replacement by mono- or diphosphines failed to occur cleanly; the reaction of complex (**5a**) with such reagents was not attempted. In our preliminary experiments it was established that its hexafluoro-analogue (**5b**) [prepared in 71% overall yield from $(C_3H_5)_2Ru\ C_8H_{12}$ via complex (**4**) and $NaC_6HF_6O_2$ in Et_2O, b.p. 150^0C / 0.05 mmHg (Kugelrohr)] reacted productively and cleanly with biphosphines, with exclusive displacement of the cyclooctadiene ligand.



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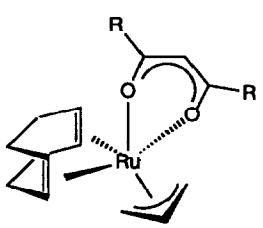
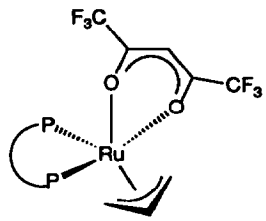


5 a R= CH_3
b R= CF_3



6 (a-g)

For preparative purposes the biphosphine and complex (**5b**) were refluxed together in equimolar amounts in degassed thf solution under argon for 5 hours, and the product normally isolated after passage through a short column of silica gel. The formation of complex (**6**) could readily be followed by in situ ^{31}P NMR spectroscopy, observing the appearance of a new AB quartet corresponding to a species with inequivalent phosphines. A particularly clean reaction ensued with 1,1'-bis(diphenylphosphino)ferrocene, and there the product (**6a**)was further recrystallised from pentane to give cubic crystals of X-ray quality. The overall structure obtained is shown in Figure 1, demonstrating that the allyl and hexafluoroacetylacetonate ligands are both η^3-coordinated. The ruthenium is then chiral leading to a racemic unit cell. The bite angle of 98^0 is comparable to that observed in related chelate complexes of 1,1'-bis(diphenylphosphino)ferrocene[8].

The conditions specified above were suitable for the preparation of a number of related biphosphine ruthenium complexes, all of which except (**6d**) were isolated in an analytically pure state. Since the ruthenium is chiral, a racemate is formed from achiral precursors, and the ^{31}P NMR reveals a single AB quartet. When an optically active biphosphine is used then two diastereomeric complexes are possible, and are characteristically produced in a 3:1 to 10:1 ratio, so that there are now two AB quartets in the ^{31}P NMR spectrum. The species formed are collated in Table 1. The BINAP derivative is exceptional in that it is formed only as a minor product in a complex spectrum in refluxing thf and its efficient formation requires 12 hours refluxing in toluene. Complexes of structure (**6a-6g**) are in general air-stable and can be stored at room temperature in the crystallime state.

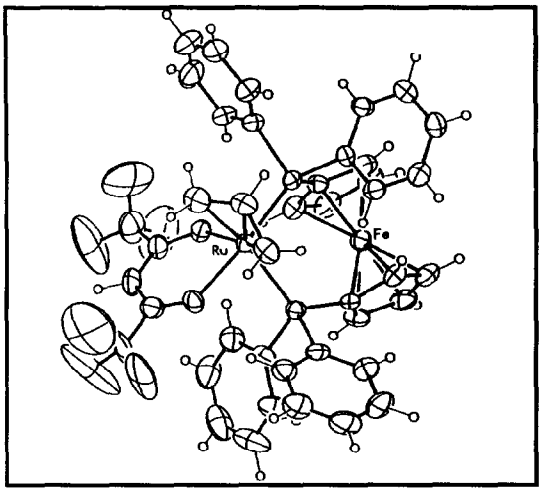


Figure 1.
X-Ray structure of compound (6a).
$C_{42}H_{32}O_2F_6P_2FeRu$, M=901.6
Monoclinic, $P2_1/c$; a=12.25, b=15.56
c=19.94; β=96.99; υ=3772Å ^{3}
R=0.060 for 4126 observed reflections
$I > 2\sigma(I)$.
Full crystallographic information has been deposited with the Cambridge database.

Ligand	^{31}P NMR major	^{31}P NMR minor	Yield %	M.p. ^{0}C
a	δ=58.5,24.5 ppm. J=34 Hz		85	153
b	δ=87.2,59.5 ppm. J=30 Hz		60	58
c	δ=58.7,16.3 ppm. J=37 Hz	δ=48.0,20.4 ppm. J=38 Hz	41	95-6
d	δ=59.7,23.6 ppm. J=36 Hz	δ=53.4,29.8 ppm. J=30 Hz	58	128-130
e	δ=54.2,12.0 ppm. J=39 Hz	δ=45.1,15.3 ppm. J=40 Hz	60	75
f	δ=51.5,36.5 ppm. (broad)	δ=49.0,36.8 ppm. (broad)	62	225
g	δ=60.8,31.1 ppm. J=37 Hz.	δ= 59.9,31.2 ppm. J=43 Hz	77	247-8

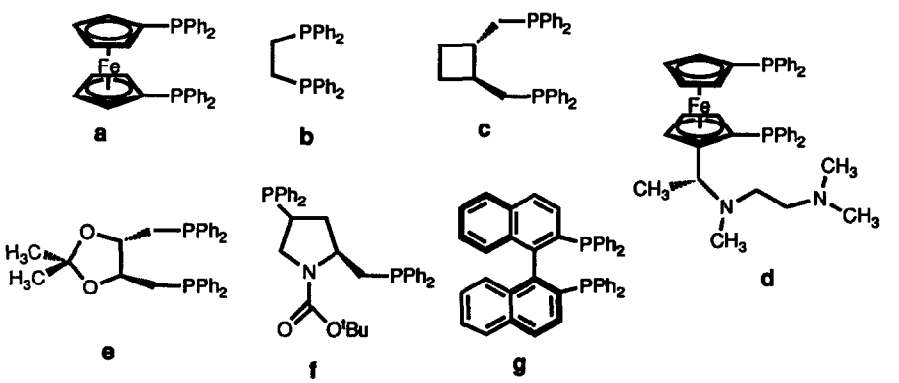


Table 1. *Synthesis and properties of complexes of type (6) from chelating biphosphines*

Complex (**6g**) and its analogues are not catalytically active for the hydrogenation of representative olefins such as tiglic and itaconic acid (4 atm H_2, thf / MeOH 1:1, 20^{0}C, 1-2 days). Several methods of activation were investigated, and treatment of the ruthenium complex with an excess of trimethylsilyl triflate in thf at reflux, followed by precipitation in pentane and thermal removal of excess reagent was shown to be effective. The orange species so produced is comparable in catalytic activity to the Ru BINAP catalysts previously described, giving hydrogenated product in 84% e.e. with tiglic acid.

A more controlled method of activation is exemplified by the reaction of complex (**6a**) with 2 equivalents of trimethylsilyl triflate in CH_2Cl_2, which results in an immediate colour change from maroon to orange. This is associated with characteristic changes in the ^1H, ^{31}P and ^{19}F NMR of the solution consistent with loss of the allyl ligand to give a highly dynamic species. The achiral complex catalyst so produced is of particular interest in the separation of catalyst-induced and substrate-induced directing effects[12], and we have observed clean hydrogenation of both methyl 3-hydroxy-2-methylenebutanoate and methyl 3-carboxymethyl-2-methylenebutanoate to the anti-isomer of product; the development of this observation will be the subject of future publications.

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