ized 4C/3e species. Both, the total π,π split (PE) as well as its through-space/through-bond partition, the degree of homoconjugational stabilization (cyclovoltammetry), and the structural details (DFT) place $\mathbf{2}^{\bullet+}$ between $\mathbf{1}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$. A limitation of the observability of σ-bishomoaromatic 4C/2e dications is manifested: If $\mathbf{2}^{2+}$ is an intermediate at all on the way from **2** to $\mathbf{12}^{2+}$, minimization of Coulomb repulsion through "hydride" elimination[17]—prohibited by the skeleton in $\mathbf{1}^{2+}$ ("*anti*-Bredt protection")[18]—wins over σ-bishomoaromaticity.

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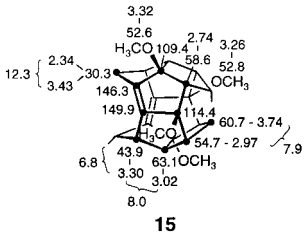
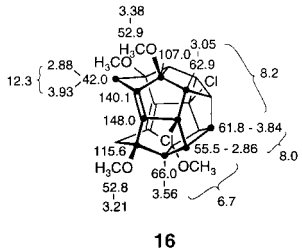



**15**




**16**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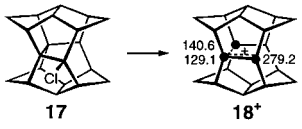
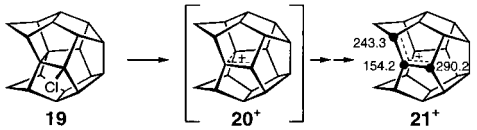



**17** **18**$^+$




**19** **20**$^+$ **21**$^+$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# A Versatile and High-Yield Route to Active and Well-Defined Catalysts [Ru(bisphosphane)(H)(solvent)$_3$](BF$_4$)**


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The well-known and well-defined Rh systems $[Rh(\widehat{P\,P})(sol)_2]^+$ ($\widehat{P\,P}$ = chiral bisphosphane ligand, sol = weakly O-bound solvent, for example acetone, THF, MeOH)[1] catalyze a wide variety of reactions, the most prominent of which is the asymmetric hydrogenation of functionalized


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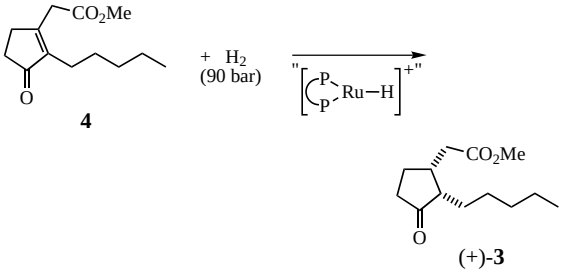
alkenes. The latter reaction is the most-studied reaction in enantioselective catalysis and has attained a high degree of maturity.[2] The versatility and efficiency of these catalysts arises to a large part from a combination of three features. They are generated cleanly and in high yield, maximizing their net activities. They readily undergo insertion reactions, two-electron oxidative additions, and reductive eliminations. They are coordinatively unsaturated, contain labile solvento ligands, and are sterically unencumbered. This combination of coordination unsaturation and low steric congestion accommodates reactions that proceed by oxidative addition of H–X (e.g. X = H for hydrogenation) as well as alkene or ketone coordination.

In the mid 1980s, the focus changed from Rh to lower costing Ru, and it is now evident that the most versatile and often the most active chiral catalysts for hydrogenation of functionalized alkenes and ketones are $[Ru^{II}(\widehat{P\,P})]$ complexes.[2] Despite this, only two of the Ru systems known prior to the present work[3] possess features that parallel those of $[Rh(\widehat{P\,P})(sol)_2]^+$, and the importance of these two may have been overlooked. Both are hydrido, monocationic complexes of the type $[Ru(\widehat{P\,P})(H)(sol)_n]^+$ ($n = 2, 3$). These cations also possess a hydride ligand, which allows for reaction pathways not directly available in the Rh systems.

The first such system, reported by the group of one of us,[4] consists of the compounds $[Ru((+)\text{-BINAP})(H)(MeCN)_n(sol)_{3-n}](BF_4)$[5a] (sol = MeOH, THF, acetone, $n = 0-3$), which catalyze the hydrogenation and hydrosilylation of functionalized C–C and ketonic C–O double bonds as well as the isomerization of olefins.[4a,c] Access to the system[4a] was established by treating the known *cis*-[Ru(1,2:5,6-$\eta$-cod)($\eta^3$-allyl)$(MeCN)_2](BF_4)$[6] (cod = 1,5-cyclooctadiene) with (+)-BINAP to give [Ru((+)-BINAP)(1,2,3:5,6-$\eta$-$C_8H_{11}$)(MeCN)]-$(BF_4)$ ($C_8H_{11}$ = 2,5-cyclooctadienyl). Hydrogenation at atmospheric pressure and room temperature generates cyclooctane and $[Ru((+)\text{-BINAP})(H)(MeCN)_n(sol)_{3-n}](BF_4)$. Since the MeCN ligand effectively blocks one coordination site, one could expect $[Ru(\widehat{P\,P})(H)(sol)_n]^+$ to be much more active in the absence of MeCN or other strongly coordinating solvents. The second of such species was reported by Pregosin et al.[7] The coordinatively unsaturated [Ru((−)-di-*t*Bu-MeOBIPHEP)$(H)(i\text{PrOH})_2](BF_4)$[5b, 7] was generated from the corresponding Takaya–Noyori precursor [Ru((−)-di-*t*Bu-MeOBIPHEP)$(OAc)_2$][8] by treatment with aqueous $HBF_4$ in *i*PrOH under 60 atm of $H_2$. It is presumably the active catalyst for Hoffmann–La Roche's unprecedented hydrogenation of a 2,5-dialkyl-3-hydroxy-$\alpha$-pyrone.[5b, 7, 9] Remarkably, this compound was characterized in the solid state by X-ray diffraction.[7] Its synthesis is arduous and starts out from an advanced precursor, however, and there are no reports of analogues containing other $\widehat{P\,P}$ prepared by this procedure.

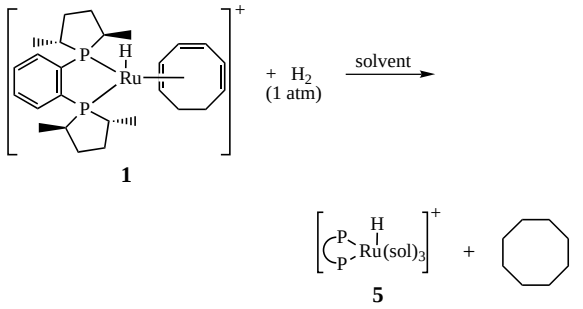
There are two reports on the dicationic complexes $[Ru(\widehat{P\,P})(sol)_4]^{2+}$, which have structures that more directly parallel $[Rh(\widehat{P\,P})(sol)_2]^+$. One is [Ru((−)-BINAP)$(MeCN)_4$]-$(BF_4)_2$,[10] which is close to catalytically inactive, presumably because the MeCN ligands are bound too strongly. The other concerns a class of catalysts formulated at one time as "$[Ru(\widehat{P\,P})](BF_4)_2$" by the Hoffmann–La Roche group, but without structural characterization.[5b, 9]

Our previous paper[3] describes the first synthesis of a new prototypal catalyst precursor, [Ru((−)-Me-DuPHOS)(H)-($\eta^6$-cot)$](BF_4)$ (**1**; cot = 1,3,5-cyclooctatriene), made in one step from [Ru(1,2:5,6-$\eta$-cod)($\eta^3$-methallyl)$_2$], (−)-Me-DuPHOS[5c] ((−)-**2**), and $HBF_4 \cdot Et_2O$. The catalyst precursor **1** was identified during the development of an industrial process for making the fragrance chemical (+)-*cis*-methyl dihydrojasmonate (+)-**3** by an enantioselective hydrogenation of the doubly functionalized, tetrasubstituted alkene **4**, a vinylogous $\beta$-oxoester [Eq. (1); the counterion $BF_4^-$ is omitted throughout].




(1)

We found that **1** reacts cleanly within minutes at ambient temperature with $H_2$ at atmospheric pressure in the appropriate solvent to afford the catalysts *fac*-[Ru((−)-Me-DuPHOS)$(H)(sol)_3](BF_4)$[11] (**5**; sol = acetone, MeOH, EtOH) and cyclooctane [Eq. (2)]. These results suggested that the

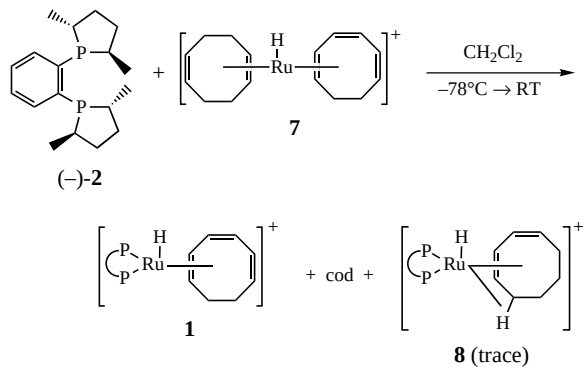



(2)

catalysts $[Ru(\widehat{P\,P})(H)(sol)_3]^+$ are generally accessible from the precursors $[Ru(\widehat{P\,P})(H)(\eta^6\text{-triene})]^+$ by hydrogenation, just as $[Rh(\widehat{P\,P})(sol)_2]^+$ are accessed from $[Rh(\widehat{P\,P})(\eta^4\text{-diene})]^+$.[1, 2]

Our first route[3] to $[Ru(\widehat{P\,P})(H)(\eta^6\text{-cot})](BF_4)$ is difficult to adapt to $\widehat{P\,P}$ other than Me-DuPHOS (**2**). We thus sought a more general, simple, and high-yielding synthesis. As reported by Chaudret and Tkatchenko et al.,[12] protonation of [Ru(1,2:5,6-$\eta$-cod)($\eta^6$-cot)] (**6**)[13] at low temperature by $HBF_4 \cdot Et_2O$[14] in $CH_2Cl_2$ generates [Ru(H)(1,2:5,6-$\eta$-cod)-($\eta^6$-cot)$](BF_4)$ (**7**), which rearranges to [Ru(H)(1-5-$\eta$-$C_8H_{11}')_2](BF_4)$ ($C_8H_{11}'$ = 2,4-cyclooctadienyl) upon warming. These authors further reported that addition of excess monodentate ligands ($H_2O$, MeCN, $MeP(Ph)_2$, $\geq 3$ equivalents) to **7** at low temperature followed by warming to ambient temperature produces [Ru(1-5-$\eta$-$C_8H_{11}')(L)_3](BF_4)$ and 1,3-cyclooctadiene (cod′).[12] We now report that addition of one equivalent of (−)-Me-DuPHOS ((−)-**2**) to **7** in $CH_2Cl_2$ at −78 °C followed by warming to ambient temperature

generates [Ru((−)-Me-DuPHOS)(H)($\eta^6$-cot)](BF$_4$) (**1**) in high yield (quantitative by NMR spectroscopy, >80% yield of isolated product) plus one equivalent of cod [Eq. (3)].




(3)

Small amounts (~3%) of [Ru((−)-Me-DuPHOS)(H)($\eta^4$-cod′)](BF$_4$) (**8**) also form,[3] which we identify and discuss below. Addition of more than one equivalent of (−)-**2** leads to the known[15] [Ru((−)-Me-DuPHOS)$_2$(H)]$^+$ by displacement of the cot ligand. Alternatively, **1** can simply be prepared by reaction between **6** and one equivalent of the easily prepared, storable monoprotio phosphonium salt (−)-**2**·HBF$_4$[3] in CH$_2$Cl$_2$ at room temperature. The yield of **1** by this procedure is ~88% (containing ~3% of **8**). Figure 1 shows the structure

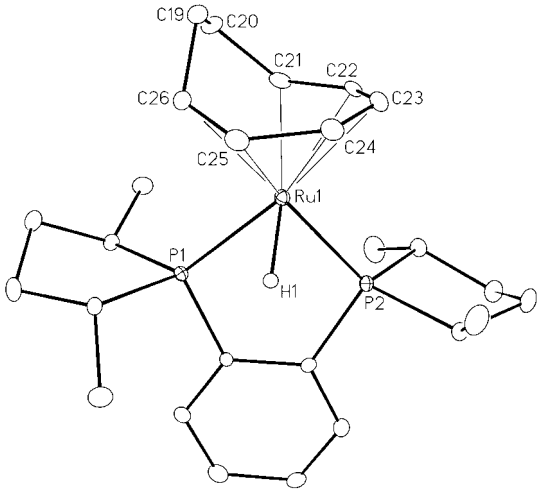
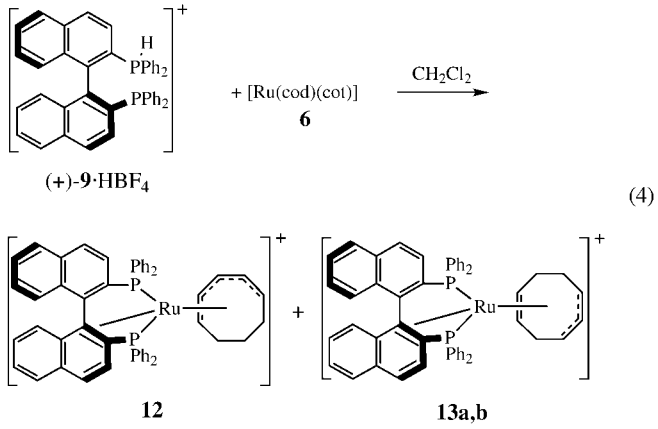



Figure 1. Structure of the cation of **1** in the crystal (all hydrogen atoms except the hydride ligand are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru-C21 2.380(5), Ru-C22 2.228(4), Ru-C23 2.265(5), Ru-C24 2.226(4), Ru-C25 2.215(5), Ru-C26 2.411(5), Ru-P1 2.305(1), Ru-P2 2.291(1), Ru-H 1.52(4), C19-C20 1.507(8), C20-C21 1.493(7), C21-C22 1.407(7), C22-C23 1.443(7), C23-C24 1.399(6), C24-C25 1.435(7), C25-C26 1.369(7); P1-Ru-P2 84.90(5), P1-Ru-H 68(2), P1-Ru-H 75(2).

of the cation of **1** as determined by X-ray diffraction, which also located the hydride ligand.[16] The Ru–H bond length (1.52(4) Å) is within the range reported for other Ru–H compounds.[7, 12, 15, 17] The geometries of the coordinated $\eta^6$-cot[12, 18] and (−)-Me-DuPHOS ((−)-**2**)[15] ligands compare well to those reported in the literature.

We have adapted this synthesis to incorporate (+)-BINAP ((+)-**9**), (+)-Tol-BINAP ((+)-**10**),[5a] and (−)-JOSIPHOS ((−)-**11**).[5d] Reaction of (+)-**9**·HBF$_4$ with **6** in CH$_2$Cl$_2$ at ambient temperature formed a mixture of [Ru((+)-BINAP)(1,2,3,4,5-$\eta$-C$_8$H$_{11}'$)](BF$_4$) (**12**; ~64%), and two diastereoisomeric [Ru((+)-BINAP)(1,2,3:5,6-$\eta$-C$_8$H$_{11}$)](BF$_4$) (**13a**, **b**) (~18% each) [Eq. (4)]. Use of (+)-**10**·HBF$_4$ gave analogous




(4)

results. Reaction of **7** with (+)-**9** or (+)-**10** at −78°C followed by warming to ambient temperature afforded a mixture consisting of **12** (~82%) and **13a**, **b** (~9% each), or the corresponding Tol-BINAP analogues. The simplest and cleanest procedure is to carry out the protonation of **6** and the subsequent reaction with (+)-**9** at ambient temperature, which yields **12** as the sole product in 86% yield. Identification of **12** and its Tol-BINAP analogue was accomplished by extensive multinuclear one- and two-dimensional NMR spectroscopy and confirmed by mass spectrometry. In these investigations, we could rely on the prior characterization of two structurally analogous cations, [Ru((−)-di-*t*Bu-MeOBIPHEP)(1,2,3,4,5-$\eta$-C$_8$H$_{11}'$)]$^+$ and [Ru((−)-*i*Pr-MeOBIPHEP)(1,2,3,4,5-$\eta$-C$_8$H$_{11}'$)]$^+$ (for which an X-ray crystal structure was provided as well) by Pregosin et al.[5b,e] In complexes of this type, the $\widehat{\text{P P}}$ ligands behave as six-electron donors by bonding to Ru through P and through $\eta^2$-coordination to one ring in the binaphthyl or biphenyl backbones.[5e, 19] Pregosin et al. prepared one of their [Ru($\widehat{\text{P P}}$)(1,2,3,4,5-$\eta$-C$_8$H$_{11}'$)]$^+$ from the same precursor [Ru((−)-di-*t*Bu-MeOBIPHEP)(OAc)$_2$] as their catalyst [Ru((−)-di-*t*Bu-MeOBIPHEP)(H)(*i*PrOH)$_2$](BF$_4$)[7] (see above), but did not report the use of [Ru($\widehat{\text{P P}}$)(1,2,3,4,5-$\eta$-C$_8$H$_{11}'$)]$^+$ as catalyst precursors. We found that the $\eta^2$-bond to the binaphthyl backbone in **12** is disrupted by excess MeCN to give [Ru($\eta^2$-(+)-BINAP)(1,2,3,4,5-$\eta$-C$_8$H$_{11}'$)(MeCN)](BF$_4$). Compounds **13a**, **b** are probably the kinetically formed products and tend to rearrange to the more stable **12**. In the BINAP/Tol-BINAP series, **12** and its analogue are presumably in equilibrium with, but more stable than, the corresponding [Ru($\widehat{\text{P P}}$)(H)($\eta^6$-cot)](BF$_4$), which is favored in the case of Me-DuPHOS.

We found that (−)-**11**·HBF$_4$ (PCy$_2$ group protonated) does not react with **6** at room temperature, suggesting that the PCy$_2$ group is too basic to allow proton transfer to **6**. Our best procedure to produce [Ru((−)-JOSIPHOS)(H)($\eta^6$-cot)](BF$_4$)

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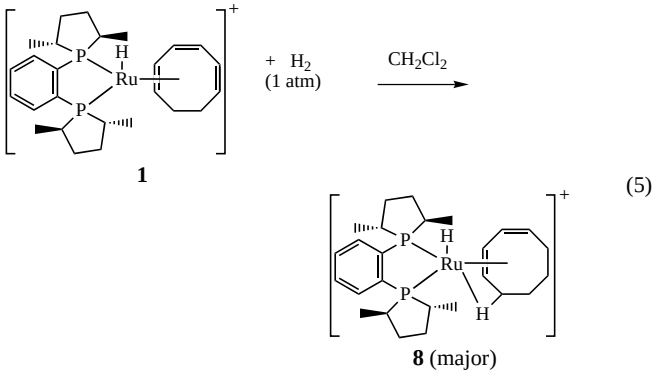
(**14**) is to treat **7** with (−)-**11** in $CH_2Cl_2$ at −25 °C and then allow the solution to warm to room temperature. This procedure gives a mixture consisting of **14** (one of two possible diastereoisomers; ~85%), plus small amounts of [Ru((−)-JOSIPHOS)(H)($\eta^4$-cod′)]($BF_4$) (**15**; ~9%) and of (−)-**11** · $HBF_4$ (~6%). The $^1$H and $^{13}$C NMR spectra of **14** and **15** are complex. The gross identification of **14**[20] is based on the diagnostic high-field signal for the hydride ligand in the $^1$H NMR spectrum, which correlates with that for **1**, the signals for the $\eta^6$-cot ligand in the $^{13}$C NMR spectrum, and the mass spectrum. The clean $^{31}$P NMR spectrum establishes the integrity of the sample. Compound **15** is identified below.

The reaction of **1** with $H_2$ in $CH_2Cl_2$ solution at atmospheric pressure and room temperature is rapid, and slows after uptake of about one equivalent of $H_2$. The major species in solution after the reaction slows is **8** [Eq. (5), one of two



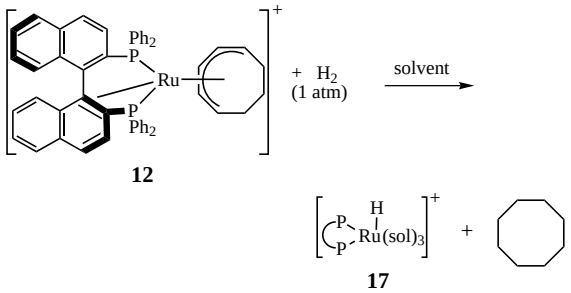

**1** (5)

**8** (major)

possible diastereoisomers]. The minor species present at this stage are cyclooctane and a number of unidentified Ru hydrides. Compound **8** is formed in near quantitative yield (NMR spectroscopy) when the hydrogenation is carried out at −40 °C. The gross structure of **8** (without assignment of the relative configuration), as determined by multinuclear one- and two-dimensional NMR spectroscopy, has cod′ coordinated to Ru through the double bonds and an allylic agostic C–H interaction. Compound **14** reacts with $H_2$ in $CH_2Cl_2$ in an analogous fashion to cleanly give **15**. The identification of **15**[20] is in part based on the diagnostic high-field $^1$H NMR signals for the hydride ligand and the agostic hydrogen atom, which correlate with those for **8**. The identities of **8** and **15** are confirmed by chemical correlation. Excess MeCN entirely displaces the cod′ ligands in **8** and **15** to give the corresponding *fac*-[Ru($\widehat{P\ P}$)(H)($MeCN)_3$]($BF_4$) complexes, whose spectral features parallel those of *fac*-[Ru((+)-BINAP)(H)-($MeCN)_3$]($BF_4$).[4a] Compounds **8** and **15** are the minor products from the preparations of **1** and **14** (see above). Their presence is of no consequence when {**1** + **8**} and {**14** + **15**} are used as hydrogenation catalyst precursors because both sets of complexes are fully reduced in donor solvents to give in each case the same catalyst.

In acetone (in which **1** is sparingly soluble: suspension), MeOH, or EtOH, hydrogenation of **1** at atmospheric pressure and room temperature quickly results in the formation of cyclooctane and **5**[11] (all are soluble in their respective solvents) in quantitative yield [Eq. (2)]. Solvent exchange is extremely rapid for these complexes. Attempts to isolate them in crystalline form failed; they are only stable in solution and consequently they were identified by NMR spectroscopy. For example, the $^1$H, $^{13}$C, and $^{31}$P NMR spectra of **5** in [$D_6$]acetone just show the corresponding signals from the bound ligand (−)-**2**, from the hydride ligand, and from cyclooctane. Brief exposure of **1** to $H_2$ in the neat substrate **4** under the conditions of the synthesis of (+)-**3**[3] [Eq. (1), ambient temperature, 90 bar, 5 min, then degassing] results in formation of a *fac*-[Ru((−)-Me-DuPHOS)(H)(**4**)$_n$]($BF_4$) (**5′**; $n = 2$ or 3), which is apparently a strict analogue of **5**, with **4** as a weakly O-bonded ligand (typical $^1$H NMR hydride signal, $^{31}$P NMR); there is no evidence of alkene coordination to Ru. Hydrogenation of **14** in neat **4** under the same conditions forms in an analogous manner two isomeric [Ru((−)-JOSIPHOS)(H)(**4**)$_n$]($BF_4$) (**16′a**, **b**; $n = 2$ or 3). [Ru((−)-JOSIPHOS)(H)($sol)_n$]($BF_4$) **16** apparently reacts further with $H_2$ in acetone; hydrogenation of **14** in [$D_6$]acetone at atmospheric pressure and ambient temperature gives a mixture of mainly four hydride species, one of which was identified as **16**. The other three could not be identified with certainty.

Acetone and THF solutions of **12** (with **13a**, **b** admixed or not) likewise react rapidly under $H_2$ gas at atmospheric pressure and room temperature to generate in quantitative (NMR) yields *fac*-[Ru((+)-BINAP)(H)($sol)_3$]($BF_4$) (**17**, sol = acetone, THF) and cyclooctane [Eq. (6)]. The magnitude of $J_{P,H}$ for all the [Ru($\widehat{P\ P}$)(H)($sol)_n$]($BF_4$) reported here and in the literature shows that the hydride ligand always occupies a coordination site mutually *cis* to the phosphorus centers.




**12** (6)

**17**

In summary, our results outline an apparently versatile synthetic route to the active catalysts [Ru($\widehat{P\ P}$)(H)($sol)_3$]$^+$.[21] Our catalyst precursors can be prepared easily, in high yield, and they can be stored for long periods at low temperature under argon. A potential limitation of our technique is the synthesis of **6**. The literature yields of this compound vary;[13] in our hands, the yield was consistently about 35%. Despite this potential limitation, our methodology certainly provides a rapid and effective means for screening [Ru($\widehat{P\ P}$)(H)($sol)_3$]$^+$ catalysts in industrial and academic environments to the degree that [Rh($\widehat{P\ P}$)($sol)_2$]$^+$ catalysts are screened today. Various improvements and variants[22] can now be envisaged, and the hydrogenation of new, more weakly binding substrates that do not react with conventional $Ru^{II}$ hydrogenation catalysts can now be explored. Our industrial processes in

which the $\beta,\gamma$-unsaturated ester **4**, neat or in very weakly donating solvents such as $CH_2Cl_2$, is hydrogenated with our catalysts,[3] constitute the first examples.

*Experimental Section*

Operations at ambient temperature were carried out in glove boxes operated with Ar or $N_2$, and operations at low temperature were carried out using standard Schlenk techniques and Ar. Operations involving $H_2$: operations at atmospheric pressure were carried out by using Schlenk techniques, and operations at 90 bar (all at ambient temperature) in open Teflon or glass tubes placed inside a stainless steel autoclave, which was charged and decharged in a glove box. NMR tubes were sealed under Ar. NMR spectra ($^1$H at 400.1 MHz, $^{13}$C at 100.6 MHz, and $^{31}$P at 161.9 MHz) were measured in $CD_2Cl_2$ at 300 K unless indicated otherwise. $H_2$ gas (99.99990 % and 99.998 %) was used as received. All solvents were distilled from appropriate drying agents under Ar.

**1** from **6** and (−)-**2**·$HBF_4$ at ambient temperature: To a stirred solution of **6** (163 mg, 0.517 mmol) in $CH_2Cl_2$ (5 mL), a solution of (−)-**2**·$HBF_4$[3] (200 mg, 0.507 mmol) in $CH_2Cl_2$ (2 mL, another 3 mL was used to rinse) was added dropwise over about 5 min. The solution was stirred for 2 h (color change from amber to red). Slow, dropwise addition of $Et_2O$ (90 mL), filtration, washing with $Et_2O$ (4 × 5 mL) and drying in vacuo afforded **1** as bright yellow microcrystals. Yield 269 mg (0.447 mmol, 88 %, containing ca. 3 % **8**). NMR spectra in $CD_2Cl_2$ and MS of **1**: see ref. [3]. In [$D_6$]acetone/$CD_2Cl_2$ (1:1, v/v), NMR evidence suggests that an equilibrium mixture (ca. 70/30) of **1** and [Ru((−)-Me-DuPHOS)(1,2,3,4,5-$\eta$-$C_8H'_{11}$)(sol)]$BF_4$ **18** is formed within minutes. Spectra for **18**. Partial $^1$H NMR: $\delta = 0.38$ (br tq, $J = 13.5$, 2.8 Hz, 1H), 0.60 (dd, $J = 6.7$, 14.3 Hz, 3H), 3.13 (m, 1H), 4.5 (br t, $J = 8.0$ Hz, 1H), 4.95 (m, 1H), 6.93 (br t, $J = 7.0$ Hz, 1H), 7.87, 7.96 (m); $^{31}$P{$^1$H} NMR: $\delta = 70.6$, 84.9 (br.).

**12** from **6** and (+)-**9** at ambient temperature: $HBF_4 \cdot Et_2O$ (90 μL, 107 mg, 0.660 mmol) was added dropwise (syringe, ∼5 min) to a stirred solution of **6** (208 mg, 0.659 mmol) in $CH_2Cl_2$ (30 mL) (dark brown coloration). After stirring for 2 h, a solution of (+)-**9** (410 mg, 0.658 mmol) in $CH_2Cl_2$ (10 mL) was added over ∼5 min while stirring. The resulting solution (maroon) was stirred another 17 h. The solvent was evaporated in vacuo, and the product precipitated as a canary yellow microcrystalline powder by adding $Et_2O$ (100 mL) to a $CH_2Cl_2$ solution (minimal quantity) of the crude product. The product was washed with $Et_2O$ (2 × 5 mL) and dried in vacuo. Yield 519 mg (0.565 mmol, 86 %). $^1$H NMR: $\delta = -0.16$ (pseudo-q, $J = 13.5$ Hz, 1H), 0.06 (pseudo-t, $J = 14.0$ Hz, 1H), 0.85 (m, 2H), 1.00 (m, 1H), 1.53 (pseudo-t, $J = 14.0$ Hz, 1H), 1.96, 2.19, 4.63 (m, 1H each), 5.45 (m, 2H), 5.95–8.30 (aromatic); $^{13}$C{$^1$H} NMR: $\delta = 18.9$, 23.2, 27.3 (s, $CH_2$), 58.5 (t, $J_{P,C} = 3.3$ Hz, CH), 64.1 (d, $J = 35.1$ Hz, aromatic C), 71.6 (d, $J_{P,C} = 19.6$ Hz, CH), 91.0, 96.2 (s, CH), 114.1 (d, $J_{P,C} = 9.5$ Hz, CH), 123–142 (aromatic); $^{31}$P{$^1$H} NMR: $\delta = -5.6$, 64.4 (d, $J_{P,P} = 44.2$ Hz); MS (electrospray ionization): isotopic cluster for $[C_{52}H_{43}P_2Ru]^+$ centered around 831 $m/z$.

{**14** + **15**} from **7** and (−)-**11**: A freshly prepared, cooled (−25 °C) solution of $HBF_4 \cdot Et_2O$ (43 μL, 51.3 mg, 0.317 mmol) in $CH_2Cl_2$ (1 mL) was added dropwise (∼5 min) to a stirred solution of **6** (100 mg, 0.317 mmol) in $CH_2Cl_2$ (10 mL) at −25 °C (dark amber coloration). After the mixture had been stirred for 20 min at −25 °C, a cooled (−25 °C) solution of (−)-**11** (1:1 EtOH–adduct, 203 mg, 0.317 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise (∼5 min) with stirring. The resulting solution was stirred at −25 °C for 2 h, allowed to warm to room temperature, and left at that temperature for 15 h (dark orange solution). The solvent was evaporated in vacuo, and the product precipitated by adding $Et_2O$ (100 mL) to a $CH_2Cl_2$ solution (minimal quantity) of the crude product. The orange brown product was washed with $Et_2O$ (2 × 5 mL) and dried in vacuo. Yield 215 mg (mixture of **14** (85 %), **15** (9 %), combined yield 202 mg (0.227 mmol, 72 %), and (−)-**11**·$HBF_4$ (6 %)). Hydride $^1$H NMR signal for **14**: $\delta = -10.30$ (pseudo-t, $J_{P,H} = 32.5$ Hz, 1H); partial $^{13}$C{$^1$H} NMR: $\delta = 92.9$, 93.1, 94.6, 96.8, (s, CH), 97.7 (br s, CH), 99.1 (s, CH); $^{31}$P{$^1$H} NMR: $\delta = 44.4$, 62.9 (d, $J_{P,P} = 26.2$ Hz); MS (electrospray ionization): isotopic cluster for $\{[C_{55}H_{55}FeP_2Ru]^+ - 2\}$[23] centered around 801 $m/z$. Spectra of **15** (obtained by hydrogenation of {**14** + **15**} in $CD_2Cl_2$ at −40 °C and atmospheric pressure (20 min)). Partial $^1$H NMR: $\delta = -19.01$(pseudo-t, $J_{P,H} = 29.0$ Hz, 1H), −5.20 (br., 1H); $^{31}$P{$^1$H} NMR: $\delta = 65.9$, 43.3 (d, $J_{P,P} = 30.5$ Hz).

Spectra of **8** (obtained by hydrogenation of **1** (+ traces of **8**) in $CD_2Cl_2$ at −40 °C and atmospheric pressure). $^1$H NMR (213 K): $\delta = -19.07$ (dd, $J_{P,H} = 34.9$, 24.9 Hz, 1H), −6.53 (br, 1H), 0.55 (dd, $J_{P,H} = 14.9$, $J_{H,H} = 6.7$ Hz, 3H), 0.77 (dd, $J_{P,H} = 15.9$, $J_{H,H} = 6.5$ Hz, 3H), 0.86 (dd, $J_{P,H} = 19.5$, $J_{H,H} = 6.8$ Hz, 3H), 0.98 (m, 1H), 1.29 (dd, $J_{P,H} = 19.1$, $J_{H,H} = 6.9$ Hz, 3H, overlapping with signal for 1H), 1.48 (m, 2H), 1.55–1.78 (m, 4H), 1.84 (m, 3H), 2.05, 2.15 (m, 1H each), 2.24–2.53 (m, 4H), 2.59, 2.68, 4.50, 5.13, 5.28, 6.37 (m, 1H each), 7.40–7.90 (m, 4H); $^{13}$C{$^1$H} NMR (213 K): $\delta = 11.3$ (s, $CH_2$), 13.1, 13.8 (s, $CH_3$), 17.9 (d, $J_{P,C} = 8.8$ Hz, $CH_3$), 18.8, 19.6 (s, $CH_2$), 19.7 (d, $J_{P,C} = 8.8$ Hz, $CH_3$), 27.2 (s, $CH_2$), 34.0 (d, $J_{P,C} = 25.2$ Hz, CH), 35.2, 35.9 (s, $CH_2$), 36.2 (d, $J_{P,C} = 5.6$ Hz, $CH_2$), 36.7 (s, $CH_2$), 39.5 (d, $J_{P,C} = 27.2$ Hz, CH), 39.7 (d, $J_{P,C} = 31.9$ Hz, CH), 44.2 (d, $J_{P,C} = 35.0$ Hz, CH), 78.8 (d, $J_{P,C} = 13.3$ Hz, CH), 79.6, 92.1, 102.4, 130.7, 130.9 (s, CH), 131.3 (d, $J_{P,C} = 13.6$ Hz, CH), 132.3 (d, $J_{P,C} = 13.6$ Hz, CH), 142.2 (d, $J_{P,C} = 38.0$ Hz, aromatic C), 142.7 (dd, $J_{P,C} = 32.0$, 8.9 Hz, aromatic C); $^{31}$P{$^1$H} NMR (213 K): $\delta = 87.2$, 92.2 (d, $J_{P,P} = 17.3$ Hz).

Spectra of **5** (obtained by hydrogenation of **1** (+ traces of **8**) in [$D_6$]acetone at room temperature and atmospheric pressure (20 min)). $^1$H NMR: $\delta = -22.29$ (pseudo-t, $J = 34.5$ Hz, 1H), 0.64 (dd, $J_{P,H} = 14.4$, $J_{H,H} = 7.1$ Hz, 3H), 0.83 (dd, $J_{P,H} = 13.2$, $J_{H,H} = 7.2$ Hz, 3H), 1.08 (dd, $J_{P,H} = 16.0$, $J_{H,H} = 7.2$ Hz, 3H), 1.19 (dd, $J_{P,H} = 16.0$, $J_{H,H} = 7.2$ Hz, 3H), 1.32, 1.78 (m, 2H each), 2.00–2.30 (m, 6H), 2.61, 7.49, 7.78 (m, 2H each); $^{13}$C{$^1$H} NMR: $\delta = 12.7$, 15.0 (s, $CH_3$), 17.6 (d, $J_{P,C} = 9.1$ Hz, $CH_3$), 18.6 (d, $J_{P,C} = 7.6$ Hz, $CH_3$), 35.7, 36.4 (s, $CH_2$), 36.5 (d, $J_{P,C} = 6.1$ Hz, $CH_2$), 37.1 (d, $J_{P,C} = 4.6$ Hz, $CH_2$), 37.6 (d, $J_{P,C} = 22.9$ Hz, CH), 38.3 (d, $J_{P,C} = 22.9$ Hz, CH), 43.1 (d, $J_{P,C} = 33.6$ Hz, CH), 129.6 (d, $J_{P,C} = 16.8$ Hz, CH), 129.9 (dd, $J_{P,C} = 16.8$, 2.7 Hz, CH), 130.5 (d, $J_{P,C} = 15.3$ Hz, CH), 130.6 (d, $J_{P,C} = 13.7$ Hz, CH); $^{31}$P{$^1$H} NMR: $\delta = 113.9$, 118.3 (d, $J_{P,P} = 34.9$ Hz).

Spectra of **5′** in neat **4** (obtained by hydrogenation of **1** in **4** at room temperature and 90 bar (5 min) and degassing). Hydride $^1$H NMR signal: $\delta = -21.81$ (br t, $J_{P,H} \sim 34.5$ Hz); $^{31}$P{$^1$H} NMR: $\delta = 113.9$, 115.6 (br d, $J_{P,P} \sim 33$ Hz).

Spectra of **16′a,b** in neat **4** (obtained by hydrogenation of {**14** + **15**} in **4** at room temperature and 90 bar (5 min) and degassing). Hydride $^1$H NMR signals: major species $\delta = -28.62$ (br t, $J_{P,H} \sim 33$ Hz), minor $\delta = -23.00$ (br.); $^{31}$P{$^1$H} NMR: major $\delta = 70.5$, 90.8 (d, $J_{P,P} = 45.8$ Hz), minor $\delta = 60.6$, 93.0 (br. d, $J_{P,P} \sim 53$ Hz).

Spectra of **17** (obtained by hydrogenation of **12** in [$D_6$]acetone at room temperature and atmospheric pressure (20 min)). $^1$H NMR: $\delta = -19.80$ (pseudo-t, $J = 30.8$ Hz, 1H), 6.3–8.0 (aromatic); $^{31}$P{$^1$H} NMR: $\delta = 71.2$, 79.7 (d, $J_{P,P} = 49.4$ Hz).

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[16] Suitable crystals of **1** were obtained by liquid–liquid diffusion of Et$_2$O into a saturated 1,2-dichloroethane solution. $C_{26}H_{39}BF_4P_2Ru$, $M_r = 601.39$, light-green plate ($0.25 \times 0.23 \times 0.05$ mm), monoclinic, space group $P2_1$, $a = 8.4489(2)$, $b = 14.2536(4)$, $c = 11.1539(3)$ Å, $V = 1315.52$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.518$ g cm$^{-3}$, $2\theta_{max} = 50.12°$, Mo$_{K\alpha}$, $\lambda = 0.71073$ Å, scan mode = $\omega$, $T = 173(2)$ K, 6640 reflections measured, 4445 independent, 4089 with $I > 2\sigma(I)$ included in refinement, absorption correction: SADABS (Sheldrick, 1996), ($\mu = 0.760$ mm$^{-1}$, max./min. transmission 1.00/0.793), direct methods structure solution using SHELXTL-V5.0, 315 parameters varied. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The hydride ligand was refined as an isotropic atom. $R(F) = 0.0349$ (observed data), $wR_2$ ($F^2$) = 0.0807 (all data). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143502. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[20] Attempts to grow suitable crystals of **14** and **15** to confirm the gross structures and to determine the exact structures by X-ray diffraction have failed to date.

[21] We recommend careful tuning at both stages when other $\widehat{PP}$ are to be incorporated into the catalyst precursors and catalysts. For example, while **17** with sol = THF could be readily generated, **5** with sol = THF could not.

[22] For example, we have developed related methodology starting out from "[Ru(H)($\eta^5$-2,4-dimethylpentadienyl)$_2$](BF$_4$)" (T. D. Newbound, L. Stahl, M. L. Ziegler, R. D. Ernst, *Organometallics* **1990**, *9*, 2962–2972); see the patents listed in footnote [9] in ref. [3]. After submission of this paper, we learned that parallel work is in print (A. Bauer, U. Englert, S. Geyser, F. Podewils, A. Salzer, *Organometallics* **2000**, *19*, 5471–5476).

[23] The cluster centered around $m/z$ 801 corresponds to the cluster expected for the cation of **14** − 2 mu (mass units). We also observe some of the cluster for the cation of **1** − 2 mu under these conditions.

# A New Photomagnetic Molecular System Based on Photoinduced Self-Assembly of Radicals**

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*Dedicated to Professor Fred Wudl on the occasion of his 60th birthday*

The synthesis and characterization of supramolecular magnetic materials based on the self-assembly of open-shell molecules are currently of great interest.[1] The construction of such solids requires that the structural subunits exhibit noncovalent interactions that can be controlled in a predictable manner. The noncovalent intermolecular interactions that have been used to date for the assembly of such molecular subunits are hydrogen bonding,[2] transition metal

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