Synthesis of Phospholyl-Bridged Heterobimetallic Ruthenium Hydrides in Combination with Zirconium and Ytterbium and the Crystal Structure of $(THF)_2Yb[\mu(\eta^5,\eta^1)\text{-}C_4Me_4P]_2Ru(H)_2(Ph_3P)_2$

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Heterobimetallic zirconium−ruthenium and ytterbium−ruthenium dihydrides, having bridging phospholyl ligands, have been obtained for the first time. Reaction of bis(η^5-tetramethylphospholyl)dichlorozirconium [$(TMP)_2ZrCl_2$] with $RuH_4(PPh_3)_3$ gave the zirconium−ruthenium heterobimetallic $Cl_2Zr[\mu(\eta^5,\eta^1)\text{-TMP}]_2\ Ru(H)_2(PPh_3)_2$. This compound was transformed into the hydridochloride $Cl_2Zr[\mu(\eta^5,\eta^1)\text{-TMP}]_2Ru(H)(Cl)(PPh_3)_2$ by the action of CCl_4. Similarly, reaction of [$(TMP)_2Yb$] with $RuH_4(PPh_3)_3$ afforded $(THF)_2Yb[\mu(\eta^5,\eta^1)\text{-TMP}]_2Ru(H)_2(PPh_3)_2$. The structure of this compound, which has been determined by X-ray crystallography, confirms the *trans* configuration of the dihydride deduced previously from NMR data. Attempts to isolate products from the reaction of [$(TMP)_2UCl_2$] or [$(TMP)_2U(BH_4)_2$] with $RuH_4(PPh_3)_3$ were unsuccessful, but NMR data show the formation of both heterobimetallic *trans*- and *cis*-ruthenium dihydride−uranium compounds $X_2U[\mu(\eta^5,\eta^1)\text{-TMP}]_2Ru(H)_2(PPh_3)_2$ ($X = BH_4$, Cl) in solution.

Introduction

Early−late heterobimetallic compounds are of current interest. The presence, in a single molecule, of an early transition metal, possessing hard Lewis-acid character, and of a soft, late transition metal in a single molecule allows the potential for cooperative behavior between the metals which could confer unusual reactivity or catalytic properties.[1] Cyclopentadienylphosphines have often been used to bridge metallic centers;[2] the recently described ytterbium−platinum, ytterbium−nickel,[3] samarium-rhodium, and uranium−molybdenum compounds have incorporated the f-elements.[4] The phospholyl ring can also be used as a bridging system because it possesses both a 5-electron ring system, analogous to that of a Cp ligand, and a σ^2,λ^3-phosphorus atom which can act as a 2-electron donor. A bis(η^5-phospholyl) complex can thus act as a chelating ligand: we have already prepared compounds where a diphosphazirconocene dichloride is linked to a metal carbonyl residue.[5] Recently, we have also prepared several π-phospholyl complexes of the f-metals,[6,7] and some heterobimetallic ruthenium−zirconium dihydrides.[8] Then, we decided to try to link bis(η^5-phospholyl)zirconium, -ytterbium, and -uranium compounds to a ruthenium hydride moiety. Here, we describe the synthesis of the first f-metal−Ru hydride heterobimetallic systems.

Results and Discussion

Synthesis of Zirconium−Ruthenium Complexes. Previously, we have been able to obtain mixed Zr−metal carbonyl species by using bis(η^5-phospholyl)dichlorozirconium as a ligand.[5] To use the recently prepared bis(η^5-phospholyl) f-element complexes[7] as bridging ligands in the same manner, we looked for a late transition metal fragment such as $RuH_2(PPh_3)_2$, which should be capable of coordinating to the lone pairs of

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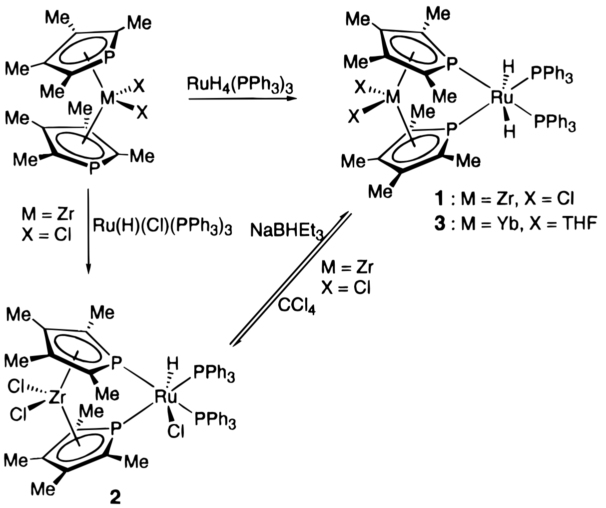
Scheme 1



the phospholyl moiety. Initially, we chose to employ bis($(\eta^5$-phospholyl)dichlorozirconium as a model system for the bis(η^5-phospholyl) f-element complexes because (a) we expected good stability for Ru−Zr(IV) complexes and (b) we had already prepared heterobimetallic ruthenium−zirconium μ-hydrido complexes,[8] wherein a flexible cyclopentadienylphosphine was used as bridging ligand.

A red solution resulted when a mixture of bis(η^5-tetramethylphospholyl)dichlorozirconium [$(TMP)_2ZrCl_2$] and $RuH_4(PPh_3)_3$ was stirred in toluene. Investigation of this solution by ^{31}P NMR showed the liberation of free PPh_3 and the progressive appearance of a deceptively simple AB quartet which, upon closer inspection, was shown to be an AA′XX′ system. This strongly suggested that the expected heterobimetallic compound had formed, that the arrangement of the phosphorus atoms around ruthenium was planar, and that the stereochemistry of the dihydride was *trans* (**1**, Scheme 1).

This hypothesis was confirmed by proton NMR, because the two equivalent hydrogen atoms bound to ruthenium were found as a quintet at −5.8 ppm with $^2J_{PH}$ of *ca.* 20 Hz, which requires that both hydrogen atoms be *cis* to the phosphine ligands. A red solid was eventually isolated and fully characterized as $Cl_2Zr[\mu(\eta^5,\eta^1)\text{-TMP}]_2Ru(H)_2(PPh_3)_2$, **1**, including by elemental analysis. H_2RuL_4 complexes generally adopt a *cis* geometry,[9] but they can also be in dynamic equilibrium with the *trans* form,[10] which has been characterized crystallographically in one instance.[11]

Reaction of **1** with CCl_4 resulted in the smooth replacement of one of the ruthenium-bound hydrogens by chlorine, with the formation of $Cl_2Zr[\mu(\eta^5,\eta^1)\text{-TMP}]_2Ru(H)(Cl)(PPh_3)_2$, **2**. This compound retains a trans arrangement of Cl and H around Ru, according to the NMR data that are similar to those of **1** except that the two sides of the phospholyl ligands are now inequivalent. This trans stereochemistry is usual for neutral Ru(II) hydride chloride complexes.[12]

Table 1. X-ray Experimental Data for 3

cryst description	deep red parallelipiped
dimens, mm	$0.20 \times 0.20 \times 0.30$
space group	orthorhombic, $P2_12_12_1$ (No. 19)
a, nm	1.3105(1)
b, nm	1.8678(2)
c, nm	2.5477(3)
V, nm^3	6.2363(1.9)
Z	4
d_{calc}	1.456
$F(000)$	2808
radiation	Mo Kα ($\lambda = 71.073$ pm)
μ, cm^{-1}	18.7
temp, K	123 ± 0.1
max 2θ, deg	60
no. of unique reflecns	9849
reflens included	5563 [$F_o^2 > 3\sigma(F_o^2)$]
corr	Lorentz−polarization, abs (DIFABS, min = 0.842, max = 1.370)
R	0.041
R_w	0.045
GOF	1.03
convergence, largest shift/error	0.02
minimization function	$w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, $w = 4F^2/\sigma^2(F^2)$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$ $\sigma^2(F^2) = \sigma^2(I) + (pF^2)^2$
instrument instability factor, p	0.05
high peak in final diff map, e·Å^{-3}	0.70(14)
low peak in final diff map, e·Å^{-3}	0.00(14)

2 was also obtained by direct reaction of $Ru(H)(Cl)(PPh_3)_3$ with $(TMP)_2ZrCl_2$, and **1** could be recovered by the back-reaction of **2** with $NaHBEt_3$.

Synthesis of a Ytterbium−Ruthenium Complex. Since the attempt to link the RuH_2 group to the phosphorus atoms of $(TMP)_2ZrCl_2$ was successful, we decided to proceed toward our goal of making a f-metal−Ru hydride heterobimetallic complex.

When $(TMP)_2Yb$[7] and $RuH_4(PPh_3)_3$ were mixed together in THF, a brown solution resulted. NMR data were also similar to that of **1**, and therefore the structure of the product was very probably that of an Yb−Ru analog of the Zr complex. Upon concentration of the solution, crystals appeared, and elemental analysis and a crystallographic study showed that the product was indeed $(THF)_2Yb[\mu(\eta^5,\eta^1)\text{-TMP}]_2Ru(H)_2(PPh_3)_2$, **3** (Scheme 1).

3 is not very stable in solution: NMR shows that a pure C_6D_6 solution of the compound slowly decomposes. Attempts to recrystallize the product after dissolution in warm THF also resulted in decomposition.

Crystal data and data collection parameters are listed in Table 1, and Table 2 lists selected bond lengths and angles; Figure 1 represents an ORTEP plot of one molecule of **3**. This figure shows distorted octahedral coordination at Ru, as is found in *trans*-$H_2Ru[P(OEt)_2Ph]_4$.[11] The Ru−P bonds are slightly shorter (0.227 nm) in this complex than in **3** (0.230 nm). The largest deviation from the ideal angle of 90° occurs for P1−Ru−P6 (81.9°), i.e. between the P atoms belonging to the $(TMP)_2Yb(THF)_2$ ligand and Ru. This emphasizes the ring strain induced by the presence of the $(TMP)_2Yb(THF)_2$ ligand in **3**, which is also reflected in the displacement of the Ru atom from the TMP mean plane (mean deviation ≈ 0.043 nm) and by the smaller centroid(TMP)−Yb−centroid(TMP) angle in **3** (122°) than in other bis(phospholyl)ytterbium complexes such as $(C_4H_2Ph_2P)_2Yb(THF)_2$ (129°).[7] The Ru−H bond (0.18 nm) is poorly defined but falls toward the high end of

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[9] Seddon, E. A.; Seddon, K. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, **1984**; p 532.

[10] E.g. see: Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1797.

[11] Guggenberger, L. J. *Inorg.Chem.* **1993**, *12*, 1317.

[12] Seddon, E. A.; Seddon, K. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984; p 543.

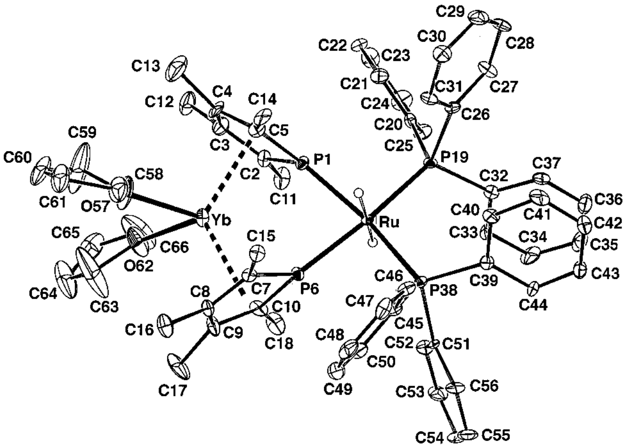


Figure 1. ORTEP plot of one molecule of **3** with ellipsoids scaled at the 50% probability level.

Table 2. Selected Bond Lengths (nm) and Angles (deg) for 3

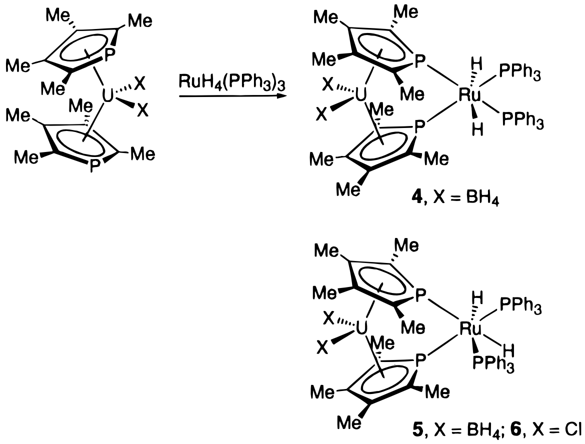
Distances			
Ru−P1	0.2296(2)	Yb−C (av)	0.276
Ru−P6	0.2288(2)	Yb−O57	0.2418(8)
Ru−P19	0.2303(2)	Yb−O62	0.2448(8)
Ru−P38	0.2299(2)	C2−P1	0.1765(9)
Ru−H1	0.18(1)	C5−P1	0.172(1)
Ru−H2	0.18(1)	C7−P6	0.1755(9)
Yb−P1	0.2930(2)	C10−P6	0.1725(9)
Yb−P6	0.2935(2)		
Angles			
P1−Ru−P6	81.82(9)	H2−Ru−P38	88(3)
P1−Ru−P19	91.15(9)	H1−Ru−H2	175(4)
P6−Ru−P38	89.16(9)	C2−P1−C5	92.2(5)
P19−Ru−P38	98.72(9)	C7−P6−C10	91.7(4)
H1−Ru−P1	89(3)	O−Yb−O	81.9(3)
H1−Ru−P19	81(3)	Cnt−Yb−Cnt	122.2
H2−Ru−P6	90(3)		

Ru−H bond distances.[13] The long distance between Yb and Ru (0.425 nm) precludes any interaction between the two metals. The other structural features (bond lengths and distances within the TMP ligand and the phenyl rings, geometry around the Yb atom) are normal.

Reactions of Phospholyluranium Derivatives with $RuH_4(PPh_3)_3$. All attempts to isolate products in the reactions of $(TMP)_2U(BH_4)_2$ and $(TMP)_2UCl_2$ with $RuH_4(PPh_3)_3$ were unsuccessful. Nevertheless, the conclusions which can be drawn from the NMR spectra of the solutions are reported below.

When equimolecular amounts of $(TMP)_2U(BH_4)_2$ and of $RuH_4(PPh_3)_3$ were mixed in C_6D_6, the progressive disappearance of the starting material, the liberation of PPh_3, and formation of a new complex were observed. Two sets of signals were seen in the NMR spectra. In the ^{31}P spectrum, the minor compound ($\approx$20%) displays pseudodoublets at 178 ppm (PPh_3 bonded to Ru) and 843 ppm (P atoms of the TMP ligand). The ^1H TMP resonances corresponding to this compound show two peaks for the α- and β-methyl groups and two broad resonances for the hydride and BH_4 protons, respectively. This product is probably $(BH_4)_2U[\mu(\eta^5,\eta^1)\text{-TMP}]_2$ [*trans*-$Ru(H)_2(PPh_3)_2$], **4**, because the spectra strongly resemble those of compounds **1** and **3**, once allowance is made for the considerable shifts of the resonances due to the paramagnetism of U(IV). The major compound

Scheme 2



4, X = BH_4

5, X = BH_4; **6**, X = Cl

displays four peaks of equal intensity in the ^{31}P spectrum at 1042 (d, J_{PP} = 210 Hz) and 860 ppm (P belonging to the TMP ligand), 250 and 110 ppm (d, J_{PP} = 210 Hz) (PPh_3 ligands). The ^1H resonances corresponding to this compound consist of eight peaks for the α- and β-methyl groups and two broad resonances for the hydride protons, one of which is very broad and is shifted to very low field (153 ppm), and a very broad resonance for the BH_4 protons. The structure of a *cis*-dihydride, such as $(BH_4)_2U[\mu(\eta^5,\eta^1)\text{-TMP}]_2[cis\text{-}Ru(H)_2(PPh_3)_2]$, **5**, is consistent with the observed NMR data, because (a) in such a structure one TMP ligand is trans to a PPh_3 ligand, and indeed a trans coupling constant is detected on the spectrum,[14] and (b) in contrast to the trans isomer, there is no element of symmetry in the molecule, which causes an inequivalence of the phosphorus atoms, of all the methyl groups, and of the two hydrides (Scheme 2).

A gray solid, which was obtained from the above solution after filtration and pentane washes, gave an NMR spectrum in C_6D_6 which showed a mixture of the desired dihydrides and numerous impurities. This solid could not be purified further.

A single compound was observed when equimolecular amounts of $(TMP)_2UCl_2$ and of $RuH_4(PPh_3)_3$ were mixed in C_6D_6. Its NMR characteristics were similar to those of the major isomer of the reaction above; thus, it is tentatively assigned the structure $Cl_2U[\mu(\eta^5,\eta^1)\text{-TMP}]_2[cis\text{-}Ru(H)_2(PPh_3)_2]$. The extremely low-field position of one of the hydride resonances (+528 ppm) might indicate an interaction of this hydride with uranium, maybe in a bridging fashion.[15]

Conclusion

We have achieved a significant advance in the field of f-element-based heterobimetallics, having been able to synthesize and structurally characterize a phospholyl-bridged Yb−Ru heterobimetallic dihydride. However, solubility problems during the isolation of the products render the preparation of these compounds difficult. We are currently trying to overcome these problems by variations of the ligand environment at the f metal.

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[13] A Ru−H bond of 1.84 Å has been found: Cotton, F. A.; Hunter, D. L.; Frenz, B. A. *Inorg. Chim. Acta* **1975**, *15*, 155.

[14] No P−P *cis* coupling constants are detected, their typical value being 15−40 Hz,[9] i.e. smaller than the line broadening induced by the paramagnetism of U (IV).

[15] Hydrides directly bonded to uranium are found below 200 ppm: Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.

Experimental Section

All reactions were performed in dry solvents under dry oxygen-free nitrogen in a Jacomex glovebox or on a vacuum line. NMR spectra were recorded on a Bruker AC200 spectrometer operating at 200.13 MHz for ^{1}H and at 81 MHz for ^{31}P. Chemicals shifts are expressed in ppm downfield from external TMS (^{1}H) and external H_3PO_4 (^{31}P). Coupling constants are expressed in hertz. Elemental analyses were performed by the "Service d'analyses du CNRS", Gif-sur-Yvette, France.

$Cl_2Zr(\mu(\eta^5,\eta^1)$-TMP$)_2RuH_2(PPh_3)_2$ (1). A solution of $(TMP)_2ZrCl_2$[16] (40 mg, 0.1 mmol) and $RuH_4(PPh_3)_3$[17] (80 mg, 0.1 mmol) in toluene (30 mL) was stirred for 6 h at room temperature. The orange reaction mixture was concentrated, and the product was precipitated slowly by adding pentane. The solution was filtered yielding 20 mg (21%) of **1**, as air-sensitive red crytals. NMR: ^{1}H (C_6D_6) δ -5.9 (ps quintet, RuH, $^2J_{HP} = 19.5$ Hz), 1.8 (m, Meα, $^3J_{HP} = 14.6$), 2.06 (s, Meβ); ^{31}P (C_6D_6) δ 61 (ps d, PPh_3, $^2J_{PPtrans} \approx 212$), 109 (ps d, PC_4Me_4, $^2J_{PPtrans} \approx 212$). Anal. Calcd for $C_{52}H_{56}Cl_2P_4Ru\,Zr$: C, 58.5; H, 5.25. Found: C, 58.2; H, 5.26.

$Cl_2Zr(\mu(\eta^5,\eta^1)$-TMP$)_2RuHCl(PPh_3)_2$ (2). Method a. A solution of $(TMP)_2ZrCl_2$ (90 mg, 0.2 mmol) and Ru(H)(Cl)$(PPh_3)_3$ (180 mg, 0.2 mmol) in toluene was stirred for 5 h at room temperature. After filtration and concentration, red crystals were formed and collected for microanalysis (ca. 45 mg, 20%). The remaining solution was concentrated and gave a second crop of pure material (according to NMR). NMR: ^{1}H (C_6D_6) δ -16.2 (ps quintet, RuH, $^2J_{HP} = 19.5$ Hz), 1.55 and 2.6 (m, Meα, $^3J_{HP} = 13.5$ Hz), 1.9 and 2.06 (s, Meβ); ^{31}P (C_6D_6) δ 33 (ps d, $^2J_{PPtrans} \approx 244$, PPh_3), 88 (ps d, PC_4Me_4, $^2J_{PPtrans} \approx 244$). Anal. Calc for $C_{52}H_{55}Cl_3P_4RuZr$: C, 56.65; H, 5.03; Cl, 9.64. Found: C, 57.05; H, 5.11; Cl, 9.72.

Method b. In an NMR tube, **1** (6 mg, 0.006 mmol) was dissolved in 0.4 mL of C_6D_6 and CCl_4 (5.5 μl, 0.006 mmol) was added. The NMR signals of **1** slowly decreased in intensity whereas the signals of **2** appeared. After 2 h, only **2** was present.

Reaction of $Cl_2Zr(\mu(\eta^5,\eta^1)$-TMP$)_2RuHCl(PPh_3)_2$ with $NaHBEt_3$. In an NMR tube, $NaHBEt_3$ (5.5 μL of a 1.1 M THF solution, 0.006 mmol) was added to a THF-d_8 solution of **2** (6 mg, 0.006 mmol). After 2 h, only **1** was present in the solution.

$(THF)_2Yb(\mu(\eta^5,\eta^1)$-TMP$)_2RuH_2(PPh_3)_2$ (3). $(TMP)_2Yb(THF)_2$[7] (16 mg, 0.035 mmol) and $RuH_4(PPh_3)_3$ (32 mg, 0.035 mmol) were dissolved in 2 mL of THF. After 2 days at room temperature, 0.2 mL of benzene was added. The reaction mixture was concentrated to 0.5 mL affording greenish brown crystals of **3** (6 mg, 28%), only soluble in THF. NMR: ^{1}H (THF-d_8) δ -6.1 (ps quintet, RuH, $^2J_{PH} = 19.5$), 1.7 (Meβ) Meα masked by THF; ^{31}P (THF-d_8) δ 70 (ps d, PPh_3, $^2J_{PPtrans} \approx 220$), 103 (ps d, PC_4Me_4, $^2J_{PPtrans} \approx 220$). Anal. Calc for $C_{60}H_{72}O_2P_4RuYb$: C, 58.91; H, 5.93. Found: C, 59.47; H, 6.06.

$(BH_4)_2U(\mu(\eta^5,\eta^1)$-TMP$)_2RuH_2(PPh_3)_3$ [*trans* (4) and *cis* (5)]. Method a. In an NMR tube, $(TMP)_2U(BH_4)_2$[18] (6 mg, 0.01 mmol) and $RuH_4(PPh_3)_3$ (10 mg, 0.01 mmol) were dissolved in 0.4 mL of C_6D_6. After 2 h of stirring, the NMR spectra showed the almost quantitative formation of both **4** (*trans*) (ca. 20%) and **5** (*cis*) (ca. 80%). NMR for **4**: ^{1}H δ -35 (m, BH_4, $W_{1/2} = 240$ Hz), -24 (d, Meα, $^3J_{HP} = 13$); -22 (RuH); 45.6 (s, Meβ); ^{31}P δ 178 (d, PPh_3, $^2J_{PPtrans} = 210$); 843 (d, PC_4Me_4, $^2J_{PPtrans} = 210$). NMR for **5**: ^{1}H (C_6D_6) δ -35.5, -24, -6.8, -2.2 (d, Meα, $^3J_{HP} = 11$), 20, 19.9, 15, 13.6 (s, Meβ), 15, 153 (RuH), -48, 110 (m, BH_4, $W_{1/2} = 240$ Hz), 5.8$-$8 (m, $RuPPh_3$); ^{31}P (C_6D_6) δ 110 (d, PPh_3, $^2J_{PPtrans} = 210$), 250 (s, PPh_3), 860 (s, PC_4Me_4), 1042 (d, PC_4Me_4, $^2J_{PPtrans} = 210$).

Method b. In an attempted preparative-scale reaction, a solution of $(TMP)_2U(BH_4)_2$ (60 mg, 0.1 mmol) and $RuH_4(PPh_3)_3$ (100 mg, 0.1 mmol) in toluene (25 mL) was stirred 20 h at room temperature. After filtration and concentration of the solution to 5 mL, the NMR spectra of an aliquot showed the presence of **4** and **5** with very few impurities. The solution was evaporated to dryness affording a gray solid. Examination of this product by NMR indicated the presence of **4** and **5** but also of ca. 20% of unidentified products, and the product could not be further purified.

$Cl_2U(\mu(\eta^5,\eta^1)$-TMP$)_2RuH_2(PPh_3)_3$ (6). In an NMR tube, $(TMP)_2UCl_2$[19] (6 mg, 0.01 mmol) and $RuH_4(PPh_3)_3$ (9 mg, 0.01 mmol) were dissolved in 0.4 mL of C_6D_6. After 30 mn, the NMR spectra showed the presence of **6** (ca. 80%). NMR: ^{1}H (C_6D_6) δ -60, -43, -24, -7.8 (m, Meα), -13,8, -7.8, 11.2, 15.4 (s, Meβ), 65, 528 (RuH); ^{31}P (C_6D_6) δ 149 (d, PPh_3, $^2J_{PPtrans} = 160$), 364 (s, PPh_3), 656 (s, PC_4Me_4), 814 (d, PC_4Me_4, $^2J_{PPtrans} = 160$).

When the crude solution was pumped off and the remaining solid dissolved for NMR analysis, the spectra revealed noticeable decomposition.

X-ray Experimental Data for 3. Crystals of **3**, $C_{60}H_{72}O_2P_4RuYb\cdot 2C_4D_8O$, fw = 1367.46, were grown at room temperature from a THF solution of the compound. Data were collected on an Enraf-Nonius CAD4 diffractometer. The compound crystallized in the noncentrosymmetric space group $P2_12_12_1$ (No. 19). The crystal structure was solved and refined using the Enraf-Nonius MOLEN software package. A Patterson map yielded a solution for the two heavy atoms, and the model was completed by successive difference Fourier maps. One of the THF solvates is highly disordered, and we were unable to locate the oxygen atom with certainty; all atoms in this ring were consequently refined as carbon. The two hydrogen atoms bonded to Ru were refined in the final least-squares stages; those connected to the organic fragments were included as fixed contributions. Anisotropic temperature factors were assigned to all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.05. The final agreement factors were $R = 0.041$, $R_w = 0.045$, and GOF = 1.03. The enantiomeric structure yielded respectively $R = 0.065$, $R_w = 0.078$, and GOF = 1.77.

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Supporting Information Available: Text describing X-ray procedures and tables of X-ray data, atom positional and thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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