Syntheses and X-ray Structures of (2,2′-Biphosphinine)-(η^5-pentamethylcyclopentadienyl)-ruthenium(I) Dimer and Ruthenium(0) Complexes

Patrick Rosa, Louis Ricard, François Mathey,* and Pascal Le Floch*

Laboratoire "Héteroéléments et Coordination", UMR CNRS 7653, Ecole Polytechnique, 91128 Palaiseau Cedex, France

Received May 30, 2000

Summary: Reduction of the [Ru(Cp)(tmbp)Cl] complex (tmbp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine) with 1 and 2 equiv of sodium naphthalenide respectively yield a dimeric [Ru(Cp*)(tmbp)]$_2$ complex and a [Ru(Cp*)-(tmbp)][Na(DME)$_2$] complex which were both structurally characterized. Trapping the Ru(0) complex with MeI, Ph_3SnCl, Me_3SnCl, or H^+ affords the corresponding Ru(II) derivatives.*

Introduction

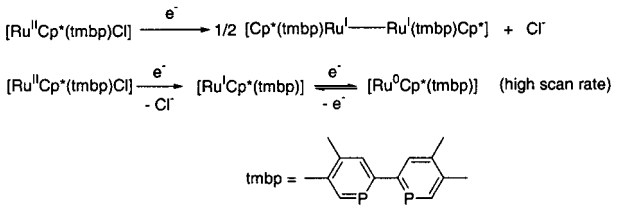
Owing to an adequate electronic balance between their poor σ-donating and their strong π-accepting abilities, phosphinines are particularly well-suited for the stabilization of low-valent and reduced transition metal complexes.[1] Some years ago, we reported the synthesis and reactivity of an (η^5-pentamethylcyclopentadienyl)chlororuthenium biphosphinine complex [Ru(Cp*)(tmbp)Cl] (Cp* = η^5-C_5Me_5) (tmbp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine) (**1**).[2] During this study, which mainly focused on the synthesis of various cationic Ru(II) derivatives, we observed that complex **1** could be electrochemically reduced to the corresponding Ru(0) complex which was found to be stable on the cyclic voltammetry time scale. Interestingly, we also noted that the outcome of this reduction was strongly dependent on the scan rate used. Thus, whereas at high scan rate (10 V s^{-1}) the Ru(0) species could be produced via two successive monoelectronic transfers, an irreversible two-electron transfer process was observed at low scan rate. On the basis of these results, we postulated the formation of a dimeric Ru(I) complex of general formula [Ru(Cp*)(tmbp)]$_2$ as intermediate in this reduction process (Chart 1).

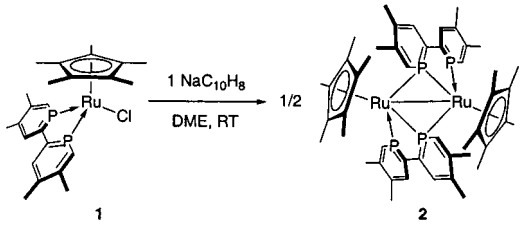
To confirm this hypothesis we investigated the chemical reduction of complex **1**. Furthermore, we were also highly interested in synthesizing and studying the synthetic potential of the Ru(0) species. Herein we report on these investigations.

Results and Discussion

As we previously reported, complex **1** was easily prepared from the reaction of the tmbp[2] ligand with [Ru(Cp*)(η^4-C_6H_{10})Cl].[3] The reduction of **1** was carried out using sodium naphthalenide as reducing agent in DME at room temperature. Whatever the solvent used, reaction of 1 equiv of NaNp with **1** yielded a very insoluble compound **2**. Due to its low solubility, **2** could not be identified by conventional NMR techniques. Fortunately, single crystals could be obtained by heating the powder obtained in hot DME (80 °C) overnight and an X-ray crystallographic study was carried out. As expected from our initial electrochemical experiments, the structure of **2** results from the formal dimerization of the [Ru(Cp*)(tmbp)] radical fragment resulting from the loss of the chloride anion (eq 1).

Chart 1





An ORTEP view of **2** is presented in Figure 1, and the most relevant bond distances and angles are listed below. Its structure is close to that of classical [M(Cp)-(η^1-CO)$_2$(μ^2-CO)$_2$] (Cp = C_5H_5, M = Fe, Ru) dimers.[4] In each biphosphinine, one phosphorus atom bridges the two Ru centers whereas the other is classically η^1-bonded. This type of bonding mode is not unprecedented. In 1992, Venanzi et al. reported the X-ray structure of a dicationic iridium(I) dimer [Ir$_2$(niphos)$_2$(COD)$_2$][SbF$_6$]$_2$ of the 2-(2′-pyridyl)phosphinine ligand (niphos) in which

(1) See, for example: (a) Mathey, F.; Le Floch, P. *Chem. Ber.* **1996**, *129*, 263. (b) Avarvari, N.; Mézailles, N.; Ricard, L.; Le Floch, P.; Mathey, F. *Science* **1998**, *280*, 1587. (c) Elschenbroich, C.; Nowontny, M.; Behrendt, A.; Massa, W.; Wocadlo, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1343.

(2) (a) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1991**, *113*, 667. (b) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *Organometallics* **1992**, *11*, 2475. (c) Rosa, P.; Mézailles, N.; Mathey, F.; Le Floch, P. *J. Org. Chem.* **1998**, *63*, 4826.

(3) Le Floch, P.; Mansuy, S.; Ricard, L.; Mathey, F.; Jutand, A.; Amatore, C. *Organometallics* **1996**, *15*, 3267.

(4) See, for example: (a) Forrow, N. J.; Knox, S. A. R. *J. Chem. Soc. Chem. Commun.* **1984**, 679. (b) Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* **1967**, *9*, 339. (c) Mague, J. T. *Acta Crystallogr.* **1995**, *C51*, 831. (d) Steiner, A.; Gornitza, H.; Stalke, D.; Edelmann, F. T. *J. Organomet. Chem.* **1992**, *431*, C21−C25. (e) Nataro, C.; Angelici, R. J. *Inorg. Chem.* **1998**, *37*, 2975.

10.1021/om0004491 CCC: $19.00
Publication on Web 11/02/2000

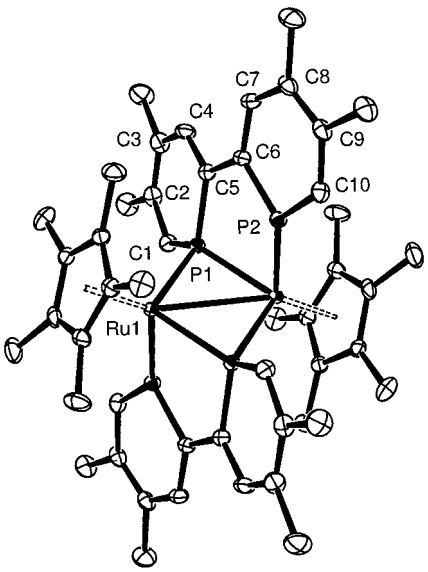
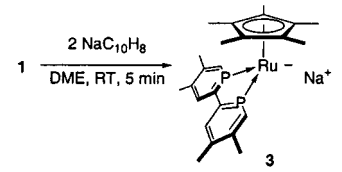


Figure 1. ORTEP drawing of complex **2**. Hydrogen atoms are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electron density. Selected bond distances (Å): Ru1−Ru1′, 2.949(1); P1−Ru1, 2.351(1); P1−Ru1′, 2.320(1); P2−Ru1, 2.227(1); P1−C1, 1.747(3); C1−C2, 1.388(4); C2−C3, 1.407(5); C3−C4, 1.392(5); C4−C5, 1.401(4); P1−C5, 1.769-(3); P2−C6, 1.745(3); C5−C6, 1.451(4); C6−C7, 1.401(4); C7−C8, 1.395(4); C8−C9, 1.413(5); C9−C10, 1.390(5); P2−C10, 1.722(3), Ru1-centroid, 1.905(3). Selected bond angles (deg): Ru1−P1−Ru1′, 78.28(3); C1−P1−C5, 101.3(2); C6−P2−C10, 104.2(2); Ru1′-Ru1−P1, 50.39(3); P1−Ru1′-P2, 96.33(3).

each phosphinine bridges the Ir_2 core in a μ^2-fashion.[5] Furthermore, very recently, the X-ray structure of a trinuclear *triangulo* Pd_3 cluster incorporating three μ^2-coordinated monophosphinines has been reported.[6] In **2**, though they are coordinated in a different fashion, both phosphinine units in tmbp nearly show the same geometrical features. A noticeable lengthening of the internal P=C bond distances is observed in both rings, as well as a shortening of the internal C−C bond of the bridge (1.451(4) vs 1.490(8) Å in the cis-free ligand).[2b] As previously noted in other tmbp complexes, this phenomenon reflects the electronic transfer from the metal to the π^* LUMO of the ligand.[7] These geometrical alterations are only limited to the PCCP unit, and no noticeable disruption of aromaticity can be observed within both rings when examining the carbocyclic backbones.

The existence of this dimer being established, we focused our work on the dielectronic reduction of complex **1**. Reaction of 2 equiv of NaNp with **1** in DME at room temperature cleanly yielded complex **3** as an oxygen-sensitive solid which was fully characterized by NMR techniques. Complex **3** displays a remarkable thermal stability, and it can be stored for days at room temperature in DME solutions. Additionally we also found that **3** could be generated from the dielectronic reduction of dimer **2** in DME at room temperature.

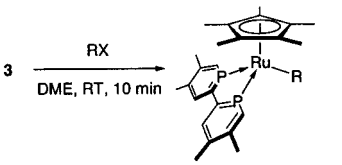


3

Additional evidence for the structure of **3** was given by an X-ray crystallographic study. Whereas some X-ray structures of anionic [Fe(Cp or Cp*)L_2] complexes (L = CO,[8a−c] P,[8d] ethylene[8e−h] or L_2 = diene[8i]) are known, to the best of our knowledge, no X-ray structures of their ruthenium counterparts have been reported so far. Complex **3** turns out to be the first example. An ORTEP view of **3** is presented in Figure 2, and important bond distances and angles are gathered below.

Complex **3** adopts a distorted three-legged piano stool structure, the ruthenium Cp* centroid axis being nearly in-plane with the tmbp ($\Theta = 170°$). The Na^+ cation only slightly interacts with the metal as shown by the Ru−Na bond distance (3.072(2) Å) which exceeds the sum of the covalent radii (2.80 Å). One may propose that the weakness of this interaction results from the steric repulsion caused by the two coordinated DME ligands. Bond lengths in phosphinine units are very close to those recorded for the [Ru(η^6-$C_{10}H_{14}$)(tmbp)] complex.[7b] As noted previously for **2**, lengthening of internal P=C bonds and a shortening of the C−C bridge point out toward an electronic transfer from the metal to the π^* LUMO of tmbp. This phenomenon is also evidenced by short Ru−P bonds (2.191(1) and 2.194(1) Å), compared to those recorded in the [Ru(Cp*)(tmbp)Cl] complex (2.2375(7) and 2.2475(7) Å).

Complex **3** is a suitable precursor of Ru(II) biphosphinine complexes. Electrophiles such as MeI, Ph_3SnCl, and Me_3SnCl cleanly react at the metal to give the expected Ru-Me **4**, Ru−SnR_3 (**5**, R = Ph; **6**, R = Me) derivatives. All of these complexes were successfully



4: R = Me (X = I)
5: R = $SnPh_3$ (X = Cl)
6: R = $SnMe_3$ (X = Cl)
7: R = H (X = MeCOO)

characterized by NMR spectroscopy and elemental analyses when possible. Additionally, we found that quenching with CH_3CO_2H yielded the Ru−H derivative **7**[9] which exhibits in ^{1}H NMR a classical hydride resonance at −14.85 ppm (t, ^2J(P−H) = 32.40 Hz).[10]

(5) Schmid, B.; Venanzi, L. M.; Gerfin, A. T.; Gramlich, V.; Mathey, F. *Inorg. Chem.* **1992**, *31*, 5117.
(6) Reetz, M.; Bohres, E.; Goddard, R.; Holthausen, M. C.; Thiel, W. *Chem. Eur. J.* **1999**, *7*, 2101.
(7) (a) Rosa, P.; Ricard, L.; Le Floch, P.; Mathey, F.; Sini, G.; Eisenstein, O. *Inorg. Chem.* **1998**, *37*, 3154. (b) Rosa, P.; Ricard, L.; Mathey, F.; Le Floch, P. *Organometallics* **1999**, *18*, 3348.

(8) See, for example: (a) Burlitch, J. M.; Hayes, S. E.; Whitwell, G. E., II *Organometallics* **1982**, *1*, 1074. (b) Petersen, R. B.; Ragosta, J. M.; Whitwell, G. E., II; Burlitch, J. M. *Inorg. Chem.* **1983**, *22*, 3407. (c) Hey-Hawkins, E.; von Schnering, H.-G. *Z. Naturforsch.* **1990**, *46b*, 621. (d) Felkin, H.; Knowles, P. J.; Meunier, B.; Mitschler, A.; Ricard, L.; Weiss, R. *J. Chem. Soc., Chem. Commun.* **1974**, 44. (e) Jonas, K.; Schiferstein, L. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 549. (f) Jonas, K.; Schiferstein, L.; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 550. (g) Jonas, J. *Adv. Organomet. Chem.*, **1981**, *19*, 97. (h) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295. (i) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843.

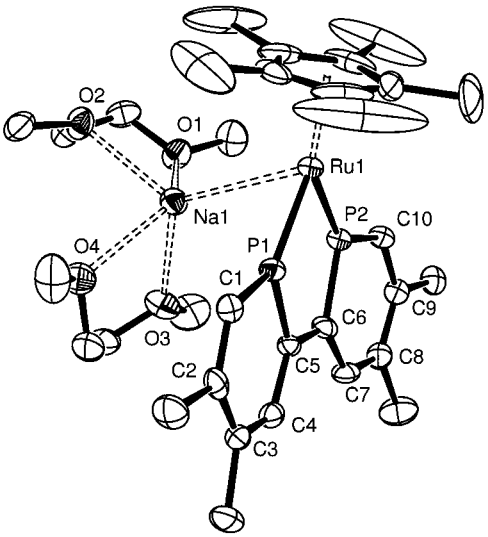


Figure 2. ORTEP drawing of complex **3**. Hydrogen atoms are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignments in the ^{13}C NMR spectrum. Selected bond distances (Å): P1−Ru1, 2.191(1); P2−Ru1, 2.194(1); P1−C1, 1.738(4); C1−C2, 1.369(6); C2−C3, 1.407(6); C3−C4, 1.400(5); C4−C5, 1.405(5); C5−P1, 1.768(4); C5−C6, 1.445(4); Ru1−Na1, 3.072(2); Na1−O1, 2.427(3); Na1−O2, 2.402(3); Na1−O3, 2.346(3); Na1−O4, 2.564(3). Bond angles (deg): P1−Ru1−P2, 78.69(4); C1−P1−C5, 101.9(2), C6−P2−C10, 101.(2); P1−Ru1−Na1, 73.19(5), P2−Ru1−Na1, 75.64(5), P1−Ru1−Ct(Cp*), 139.41; P2−Ru1−Ct(Cp*), 140.38.

In conclusion, we have shown that reduction of complex **1** effectively proceeds via the formation of dimer **2**. Most importantly, we also demonstrated that biphosphinine can efficiently stabilize the anionic $[Ru(Cp^*)]^-$ fragment. Further studies now focus on the reactivity of this anion.

Experimental Section

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry Et_2O, THF, DME, and hexanes were obtained by distillation from Na/benzophenone and dry CH_2Cl_2 from P_2O_5. Deuterated solvents were dried with 4 Å Linde molecular sieves. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^1H and ^{13}C NMR chemical shifts (ppm); ^{31}P NMR chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; p, pentuplet; v, virtual. IR data were collected on a Perkin-Elmer 297 spectrometer. Mass spectra were obtained at 70 eV with a HP 5989B spectrometer coupled to a HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the "Service d'analyze du CNRS", at Gif sur Yvette, France. 4,4′,5,5′-Tetramethyl-2,2′-biphosphinine[2] and complex **1** were prepared according to reported procedures.[3]

Synthesis of $[Ru(Cp^*)(tmbp)]_2$ (2). A solution of sodium naphthalenide in DME (10 mL, 0.5 mmol) was added to solid complex **1** (0.26 g, 0.5 mmol) in the glovebox at room temperature. After 1 h the volume of solvent was reduced to 5 mL, and complex **2** precipitated overnight. Filtration and washings with THF (2 × 5 mL) allowed the elimination of naphthalene and the major part of NaCl salts. After drying, **2** was recovered as a dark oxygen-sensitive powder. The presence of traces of NaCl salts precluded calculation of a precise yield. Suitable crystals for the X-ray crystallographic study were obtained by heating the powder obtained in a sealed tube in DME at 80 °C overnight. Complex **2** was too insoluble to be characterized by conventional ^1H and ^{13}C NMR techniques. IR (KBr): n, 1636 (br), 1557 (s), 1360 (s), 1360 (s), 1304 (s), 1262 (s), 1081 (s), 998 (s), 686 (s), 670 (s) cm^{-1}. Anal. Calcd for $C_{48}H_{62}P_4Ru_2$: C, 59.74; H, 6.48. Found: C, 60.05; H, 6.63.

Synthesis of $[Ru(Cp^*)(tmbp)][Na(DME)_2]$ (3). A solution of sodium naphthalenide in DME (20 mL, 1 mmol) was added to solid complex **1** (0.26 g, 0.5 mmol) in the glovebox at room temperature. After 5 min of stirring, a control by ^{31}P NMR indicated the complete formation of complex **3**. After filtration, the solvent was evaporated, and naphthalene was sublimed to yield **3** as a deep-purple oxygen- and moisture-sensitive powder. The overall yield of the reaction could not be estimated since NaCl salts could not be totally eliminated. Suitable crystals for the X-ray crystallographic study were obtained by heating the resulting deep-purple powder at 80 °C overnight in a sealed tube in a mixture of DME/Et_2O. ^{31}P NMR (C_4D_8O): δ 184.40. ^1H NMR (C_4D_8O): δ 2.23 (t, 15H, ^4J(P−H) = 1.80, Me of Cp*), 2.27 and 2.42 (s, 2 × 6H, Me of $C_{14}H_{16}P_2$), 7.70 (m, AA′XX′, 2H, ΣJ(P−H) = 26.85, $H_{3,3'}$ of $C_{14}H_{16}P_2$), 8.12 (m, AA′XX′, 2H, ΣJ(P−H) = 17.10, $H_{6,6'}$ of $C_{14}H_{16}P_2$). ^{13}C NMR (C_4D_8O): δ 13.65 (s, Me of Cp*), 22.55 (s, Me of $C_{14}H_{16}P_2$), 24.55 (vt, AXX′, ΣJ(P−C) = 8.85, Me of $C_{14}H_{16}P_2$), 87.75 (t, ^2J(P−C) = 2.65, C_{ipso} of Cp*), 115.95 (vt, AXX′, ΣJ(P−C) = 14.00, $C_{5,5'}$ or $C_{4,4'}$ of $C_{14}H_{16}P_2$), 126.70 (vt, AXX′, ΣJ(P−C) = 20.40, $C_{3,3'}$ or $C_{6,6'}$ of $C_{14}H_{16}P_2$), 129.00 (vt, AXX′, ΣJ(P−C) = 15.85, $C_{6,6'}$ or $C_{3,3'}$ of $C_{14}H_{16}P_2$), 135.70 (vt, AXX′, ΣJ(P−C) = 73.65, $C_{2,2'}$ of $C_{14}H_{16}P_2$), 139.00 (vt, AXX′, ΣJ(P−C) = 11.20, $C_{5,5'}$ or $C_{4,4'}$ of $C_{14}H_{16}P_2$). Complex **3** turned out to be too moisture- and oxygen-sensitive to be characterized by elemental analysis.

Synthesis of [Ru(Cp*)(tmbp)Me] (4). Methyl iodide (32 μL, 0.5 mmol) was added at room temperature to a solution of anion **3** prepared as described above from complex **1** (0.26 g, 0.5 mmol) and naphthalene sodium. After 5 min of stirring, a ^{31}P NMR control indicated the complete formation of **4**. The solvent was evaporated, dichloromethane (40 mL) was added, and the resulting solution was filtrated. After evaporation of dichloromethane, the resulting dark solid obtained was washed with hexanes (15 mL) and Et_2O (15 mL). Traces of naphthalene were totally removed by drying the powder obtained overnight. Complex **4** was finally isolated as a dark-red oxygen- and moisture-sensitive solid. Yield: 125 mg (50%). ^{31}P NMR (CD_2Cl_2): δ 237.30. ^1H NMR (CD_2Cl_2): δ −1.15 (t, 3H, ^3J(P−H) = 5.60, Ru-Me), 1.98 (t, 15H, ^4J(P−H) = 2.30, Me of Cp*), 2.37 (vd, AA′XX′, 6H, ΣJ(P−H) = 3.50, Me of $C_{14}H_{16}P_2$), 2.47 (s, 6H, Me of $C_{14}H_{16}P_2$), 7.97 (vd, AA′XX′, 2H, ΣJ(P−H) = 25.05, $H_{3,3'}$ of $C_{14}H_{16}P_2$), 8.20 (vd, AA′XX′, 2H, ΣJ(P−H) = 17.25, $H_{6,6'}$ of $C_{14}H_{16}P_2$). ^{13}C NMR (CD_2Cl_2): δ −21.80 (t, ^2J(P−C) = 13.50, Ru-Me), 10.95 (s, Me of Cp*), 22.30 (s, Me of $C_{14}H_{16}P_2$), 24.15 (vt, AXX′, ΣJ(P−C) = 9.00, Me of $C_{14}H_{16}P_2$), 95.40 (t, ^2J(P−C) = 2.90, C_{ipso} of Cp*), 127.90 (vt, AXX′, ΣJ(P−C) = 19.80, $C_{5,5'}$ or $C_{4,4'}$ of $C_{14}H_{16}P_2$), 129.20 (m, AXX′, ΣJ(P−C) = 40.55, $C_{3,3'}$ of $C_{14}H_{16}P_2$), 135.60 (vt, AXX′, ΣJ(P−C) = 17.35, $C_{6,6'}$ of $C_{14}H_{16}P_2$), 144.10 (vt, AXX′, ΣJ(P−C) = 13.60, $C_{5,5'}$ or $C_{4,4'}$ of $C_{14}H_{16}P_2$), 148.65 (vt, AXX′, ΣJ(P−C) = 68.25, $C_{2,2'}$ of $C_{14}H_{16}P_2$).

(9) Personal communication from Prof. R. Morris: complex **7** was previously synthesized by reduction of complex **1**. Fong, T. Ph.D. Thesis, University of Toronto, Canada, 1999.

(10) For selected references, see: (a) Jia, G.; Morris, R. *Inorg. Chem.* **1990**, *29*, 582. (b) Jia, G.; Lough, A. J.; Morris, R. *Organometallics* **1992**, *11*, 161. (c) Keady, M. S.; Koola, J.; Ontko, A. C.; Merwin, R. K.; Roddick, D. M. *Organometallics* **1992**, *11*, 3417. (d) Lemke, F.; Brammer, L. *Organometallics* **1995**, *14*, 3980. (e) Brammer, L.; Klooster, W. T.; Lemke, F. R. *Organometallics* **1996**, *15*, 1721.

Table 1. Crystallographic Data and Experimental Parameters for the Structures of 2 and 3

	2	3
mol formula	$C_{48}H_{62}P_4Ru_2$	$C_{32}H_{51}NaO_4P_2Ru$
mol wt	482.50	685.73
cryst descripn habit/size (mm))	red plate	deep purple needle
	0.18 × 0.18 × 0.16	0.22 × 0.10 × 0.08
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
a (Å)	10.778(5)	10.629(5)
b (Å)	10.920(5)	17.561(5)
c (Å)	11.546(5)	18.872(5)
α (deg)	67.620(5)	
β (deg)	69.280(5)	
γ (deg)	61.900(5)	
V (Å^3)	1082.8(8)	3523(2)
Z	2	4
D (g/cm^3)	1.480	1.293
F(000)	498	1440
μ (cm^{-1})	0.878	0.580
T (K)	150.0(1)	150.0(1)
max θ (deg)	27.47	28.28
hkl ranges	−13 to +13; −14 to +14; −14 to +11	−13 to +13; −22 to +23; −25 to +12
no. of rflns measd	6926	16433
no. of indep rflns	4887	7787
no. of rflns used	4370	6237
R_{int}	0.0247	0.0577
refinement type	F_{sqd}	F_{sqd}
H atoms	mixed	mixed
no. of params refined	253	374
Flack param	not applicable	0.52(3)
rfln/param ratio	17	16
wR2	0.1228	0.0873
R1	0.0380	0.0402
criterion	$>2\sigma(I)$	$>2\sigma(I)$
GOF	1.002	1.018
diff peak/hole (eÅ^3)	3.861(0.115/ -0.934(0.115)[a]	0.623(0.105)/ -0.461(0.105)

[a] Located approximately 0.9 Å from Ru.

Anal. Calcd for $C_{25}H_{34}P_2Ru$: C, 60.35; H, 6.89. Found: C, 60.00; H, 6.83.

Synthesis of [Ru(Cp*)(tmbp)SnPh$_3$] (5). The procedure for the synthesis of **5** is identical to that described above. Complex **5** was obtained by addition of Ph_3SnCl (0.5 mmol) to a solution of anion **3** (0.5 mmol). Complex **5** was isolated as a dark-red solid. Yield: 170 mg (70%). ^{31}P NMR ($CDCl_3$): δ 224.15 ($^2J(^{117/119}Sn-P)$ = 325.60 and 340.10). ^{1}H NMR ($CDCl_3$): δ 1.98 (t, 15H, ^4J(P−H) = 4.60, Me of Cp*), 2.30 (vd, AA′XX′, 6H, ΣJ(P−H) = 3.85, Me of $C_{14}H_{16}P_2$), 2.54 (s, 6H, Me of $C_{14}H_{16}P_2$), 6.97−7.12 (m, 15H, $SnPh_3$), 7.68 (vd, AA′XX′, 2H, ΣJ(P−H) = 19.50, $H_{3,3'}$ of $C_{14}H_{16}P_2$), 8.12 (vd, AA′XX′, 2H, ΣJ(P−H) = 24.15, $H_{6,6'}$ of $C_{14}H_{16}P_2$); ^{13}C NMR ($CDCl_3$): δ 12.55 (s, Me of Cp*), 22.85 (s, Me of $C_{14}H_{16}P_2$), 25.20 (vd, AXX′, ΣJ(P−C) = 9.80, Me of $C_{14}H_{16}P_2$), 94.80 (t, ^2J(P−C) = 2.10, C_{ipso} of Cp*), 126.90 (s, C_{para} of Ph), 127.35 (s, $^2J(^{117/119}Sn-C)$ = 23.70, C_{ortho} of Ph), 128.35 (vd, AXX′, ΣJ(P−C) = 20.95, $C_{5,5'}$ or $C_{4,4'}$ of $C_{14}H_{16}P_2$), 129.90 (m, AXX′, ΣJ(P−C) = 28.40, $C_{3,3'}$ of $C_{14}H_{16}P_2$), 136.35 (m, AXX′, ΣJ(P−C) = 27.70, $C_{6,6'}$ of $C_{14}H_{16}P_2$), 137.70 (s, $^3J(^{117/119}Sn-C)$ =33.70, C_{meta} of Ph), 144.55 (m, AXX′, ΣJ(P−C) = 19.50, $C_{4,4'}$ or $C_{5,5'}$ of $C_{14}H_{16}P_2$), 146.35 (s, C_{ipso} of Ph), 148.45 (m, AXX′, ΣJ(P−C) = 74.00, $C_{2,2'}$ of $C_{14}H_{16}P_2$. MS (m/z, rel. intensities): 833 (8, M$^+$), 483 (100, M$^+$ − $SnPh_3$). Anal. Calcd for $C_{42}H_{46}P_2$-RuSn: C, 60.59; H, 5.57. Found: C, 60.80; H, 5.63.

Synthesis of [Ru(Cp*)(tmbp)SnMe$_3$] (6). The procedure for the synthesis of **6** is identical to that described above. Complex **6** was obtained by addition of Me_3SnCl (0.5 mmol) to a solution of anion **3** (0.5 mmol). Complex **5** was isolated as a dark-red oxygen-sensitive solid. Yield: 160 mg (50%). ^{31}P NMR (CD_2Cl_2): δ 226.05 ($^2J(^{117/119}Sn-P)$ = 296.75); ^{1}H NMR ($CDCl_3$): δ −0.53 (s, 9H, $^2J(^{117/119}Sn-H)$ = 39.85 and 41.65, Me of $SnMe_3$), 2.12 (t, 15H, ^4J(P−H) = 2.30, Me of Cp*), 2.38 (vd, AA′XX′, 6H, ΣJ(P−H) = 3.50, Me of $C_{14}H_{16}P_2$), 2.49 (s, 6H, Me of $C_{14}H_{16}P_2$), 7.87 (vd, AA′XX′, 2H, ΣJ(P−H) = 24.30, $H_{3,3'}$ of $C_{14}H_{16}P_2$), 8.23 (vd, AA′XX′, 2H, ΣJ(P−H) = 19.50, $H_{6,6'}$ of $C_{14}H_{16}P_2$). ^{13}C NMR (CD_2Cl_2): δ −7.95 (t, ^3J(P−C) = 1.90, Me of $SnMe_3$), 12.10 (s, Me of Cp*), 22.35 (s, Me of $C_{14}H_{16}P_2$), 24.35 (vd, AXX′, ΣJ(P−C) = 10.50, Me of $C_{14}H_{16}P_2$), 94.50 (t, ^2J(P−C) = 2.35, C_{ipso} of Cp*), 127.20 (vd, AXX′, ΣJ(P−C) = 20.35, $C_{4,4'}$ or $C_{5,5'}$ of $C_{14}H_{16}P_2$), 128.95 (m, AXX′, ΣJ(P−C) = 27.10, $C_{3,3'}$ of $C_{14}H_{16}P_2$), 134.70 (vt, AXX′, ΣJ(P−C) = 25.20, $C_{6,6'}$ of $C_{14}H_{16}P_2$), 144.30 (vt, AXX′, ΣJ(P−C) = 17.75, $C_{5,5'}$ or $C_{4,4'}$ of $C_{14}H_{16}P_2$), 147.00 (vt, AXX′, ΣJ(P−C) = 72.15, $C_{2,2'}$ of $C_{14}H_{16}P_2$). MS (m/z, rel. intensities): 631 (13, M$^+$ − Me), 483 (30, M$^+$ − $SnMe_3$), 165 (100, $SnMe_3^+$). Anal. Calcd for $C_{27}H_{40}P_2$-RuSn: C, 50.17; H, 6.24. Found: C, 49.85; H, 6.18.

Synthesis of [Ru(Cp*)(tmbp)H] (7). The procedure for the synthesis of **7** is identical to that described above. Complex **7** was obtained by addition of CH_3CO_2H (32 μL, solution 90% in water, 0.5 mmol) to a solution of anion **3** (0.5 mmol). Complex **7** was isolated as a dark-red solid. Yield: 145 mg (60%). ^{31}P NMR (CD_2Cl_2): δ 227.80. ^{1}H NMR ($CDCl_3$): δ −14.85 (t, 1H, ^2J(P −H) = 32.40, Ru−H), 2.20 (t, 15H, ^4J(P−H) = 2.20, Me of Cp*), 2.36 (vd, AA′XX′, 6H, ΣJ(P−H) = 3.60, Me of $C_{14}H_{16}P_2$), 2.48 (s, 6H, Me of $C_{14}H_{16}P_2$), 8.04 (vd, AA′XX′, 2H, ΣJ(P−H) = 24.70, $H_{3,3'}$ of $C_{14}H_{16}P_2$), 8.17 (vd, AA′XX′, 2H, ΣJ(P−H) = 18.45, $H_{6,6'}$ of $C_{14}H_{16}P_2$). ^{13}C NMR (CD_2Cl_2): δ 12.35 (s, Me of Cp*), 22.25 (s, Me of $C_{14}H_{16}P_2$), 24.15 (m, AXX′, ΣJ(P−C) = 14.80, Me of $C_{14}H_{16}P_2$), 96.05 (t, ^2J(P−C) = 2.45, C_{ipso} of Cp*), 127.20 (vt, AXX′, ΣJ(P−C) = 19.45, $C_{4,4'}$ or $C_{5,5'}$ of $C_{14}H_{16}P_2$), 128.90 (m, AXX′, ΣJ(P−C) = 28.55, $C_{3,3'}$ of $C_{14}H_{16}P_2$), 135.30 (vt, AXX′, ΣJ(P−C) = 21.95, $C_{6,6'}$ of $C_{14}H_{16}P_2$), 143.95 (vt, AXX′, ΣJ(P−C) = 20.45, $C_{5,5'}$ or $C_{4,4'}$ of $C_{14}H_{16}P_2$), 147.45 (vt, AXX′, ΣJ(P−C) = 70.20, $C_{2,2'}$ of $C_{14}H_{16}P_2$). Complex **7** did not give reproducible elemental analysis data.

X-ray Crystallographic Studies of 2 and 3. Crystals suitable for X-ray diffraction were obtained by heating crude powders in DME at 80 °C under vacuum in a sealed tube. The tube was broken in the glovebox, crystals were protected with paratone oil for handling and then submitted to X-ray diffraction analysis. Data were collected on a Nonius Kappa CCD diffractometer using an Mo Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The structure of complex **3** was refined as a racemic twin. The crystal structures were solved using SIR 97[11] and Shelxl-97.[12] ORTEP drawings were made using ORTEP III for Windows.[13]

Acknowledgment. The authors thank the CNRS and the Ecole Polytechnique for supporting this work.

Supporting Information Available: Listings of atomic coordinates, including H atoms and equivalent isotropic displacement parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0004491

(11) SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single-crystal data: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R.

(12) Sheldrick, G. M. SHELXL-97; Universität Göttingen, Göttingen, Germany, 1997.

(13) ORTEP-3 program created by Louis J. Farrugia (Department of Chemistry, University of Glasgow).