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Synthesis and Characterization of 1,1′-Diphospharuthenocenes

Masamichi Ogasawara,* Takashi Nagano, Kazuhiro Yoshida, and Tamio Hayashi*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

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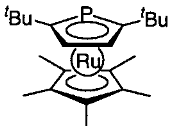
*Summary: Reaction of [RuCl$_2$(cod)]$_n$ (cod = 1,5-cyclooctadiene) with lithium 2,5-dialkylphospholide or 1-stannyl-2,5-dialkylphosphole gives Ru(η^5-PC$_4$H$_2$-2,5-R$_2$)$_2$ (R = (−)-menthyl, **4a**; or cyclohexyl, **4b**). Steric bulkiness of the R groups is a crucial factor for the successful preparation of the 1,1′-diphospharuthenocenes. The structure of the complex **4b** was studied by X-ray single-crystal structure determination, which clarified the distance between the nearly planar η^5-phospholyl ligand and the ruthenium center in the complex, being 1.811 Å.*

Introduction

Phospholyl (phosphacyclopentadienyl) anions show a variety of coordination modes and are interesting subjects for coordination chemistry.[1] Since Mathey's first discovery of monophosphaferrocene in 1977[2] and 1,1′-diphosphaferrocene in 1978,[3] many (η^5-phospholyl)iron(II) complexes have been prepared and they have provided rich and diverse chemistry in this field.[1,4] On the other hand, investigations on (η^5-phospholyl)ruthenium(II) complexes, heavier homologues of the phosphaferrocenes, have received little attention. The first report on this class of compounds, (η^5-C$_5$Me$_5$)Ru(η^5-PC$_4$H$_2$-2,5-^{t}Bu$_2$) (**1**), appeared in 1994.[5] More recently, a (η^5-PC$_4$Me$_4$)Ru(II) moiety was reported as substructures in a cationic triple-decker iron(II)−ruthenium(II) complex (**2**)[6] and half-sandwich complexes (**3**).[7] Several (η^5-polyphosphacyclopentadienyl)ruthenium(II) species have been reported as well.[8,9] Here we wish to report the synthesis and characterization of 1,1′-diphospharuthenocenes Ru(η^5-PC$_4$H$_2$-2,5-R$_2$)$_2$ (R = (−)-menthyl, **4a**; R = cyclohexyl, **4b**), which are the first examples of homoleptic phospholyl-Ru(II) complexes. The single-crystal X-ray diffraction study of **4b** clarified the molecular structure of the diphospharuthenocene.



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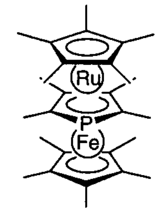

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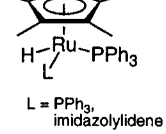

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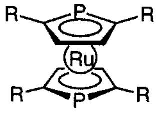

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Results and Discussion

The reaction of [RuCl$_2$(cod)]$_n$ and lithium 2,5-di((−)-menthyl)phospholide (**6a**; 2 equiv to Ru) in THF led to the formation of a pale yellow 1,1′-diphospharuthenocene Ru[η^5-PC$_4$H$_2$-2,5-((−)-menthyl)$_2$]$_2$ (**4a**) in 69% yield (Scheme 1, method A). The phosholide **6a** was generated from a corresponding 1-phenylphosphole **5a**[10] by treatment with 2 equiv of lithium metal, and co-generated phenyllithium was selectively quenched with anhydrous AlCl$_3$[11] prior to the reaction with [RuCl$_2$(cod)]$_n$. It was found that 1-tributylstannyl-2,5-di((−)-menthyl)phosphole **7a** was also effective as a phospholyl transfer reagent for the synthesis of **4a** (Scheme 1, method B). The stannylphosphole **7a** was readily prepared in situ according to a sequence illustrated in Scheme 1[12] and used for the diphospharuthenocene synthesis without

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(1) (a) Mathey, F.; Fischer, J.; Nelson, J. H. *Struct. Bonding* **1983**, *55*, 153. (b) Mathey, F. *New J. Chem.* **1987**, *11*, 585. (c) Mathey, F. *J. Organomet. Chem.* **1990**, *400*, 149. (d) Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1.

(2) (a) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1977**, *99*, 3537. (b) Mathey, F. *J. Organomet. Chem.* **1977**, *139*, 77.

(3) (a) de Lauzon, G.; Mathey, F.; Simalty, M. *J. Organomet. Chem.* **1978**, *156*, C33. (b) de Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 994. (c) de Lauzon, G.; Deschamps, B.; Mathey, F. *Nouv. J. Chim.* **1980**, *4*, 683.

(4) For the recent application of phosphaferrocenes to organic synthesis, see: (a) Ganter, C.; Kaulen, C.; Englert, U. *Organometallics* **1999**, *18*, 5444. (b) Shintani, R.; Lo, M. M.-C.; Fu, G. C. *Org. Lett.* **2000**, *2*, 3695. (c) Tanaka, K.; Qiao, S.; Tobisu, M.; Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 9870. (d) Sava, X.; Ricard, L.; Mathey, F.; Le Floch, P. *Organometallics* **2000**, *19*, 4899. (e) Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2001**, *20*, 3913.

(5) Carmichael, D.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1167.

(6) (a) Herberich, G. E.; Ganter, B. *Organometallics* **1997**, *16*, 522. (b) Herberich, G. E.; Ganter, B.; Englert, U. *Struct. Chem.* **1998**, *9*, 359.

(7) Desmurs, P.; Dormond, A.; Nief, F.; Baudry, D. *Bull. Soc. Chim. Fr.* **1997**, *134*, 683.

(8) (a) Scherer, O. J.; Brück, T.; Wolmershäuser, G. *Chem. Ber.* **1988**, *121*, 927. (b) Hitchcock, P. B.; Matos, R. M.; Nixon, J. F. *J. Organomet. Chem.* **1993**, *462*, 319. (c) Hitchcock, P. B.; Nixon, J. F.; Matos, R. M. *J. Organomet. Chem.* **1995**, *490*, 155. (d) Rink, B.; Scherer, O. J.; Wolmershäuser, G. *Chem. Ber.* **1995**, *128*, 71. (e) Hitchcock, P. B.; Johnson, J. A.; Nixon, J. F. *Organometallics* **1995**, *14*, 4382.

(9) Diphosphastibolyl-Ru(II) complexes are also known. See: (a) Francis, M. D.; Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Malik, K. M. A. *Chem. Commun.* **1996**, 1591. (b) Black, S. J.; Francis, M. D.; Jones, C. *J. Chem. Soc., Dalton Trans.* **1997**, 2183.

(10) Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2001**, *20*, 1014.

(11) Mathey, F.; de Lauzon, G. *Organomet. Synth.* **1986**, *3*, 259.

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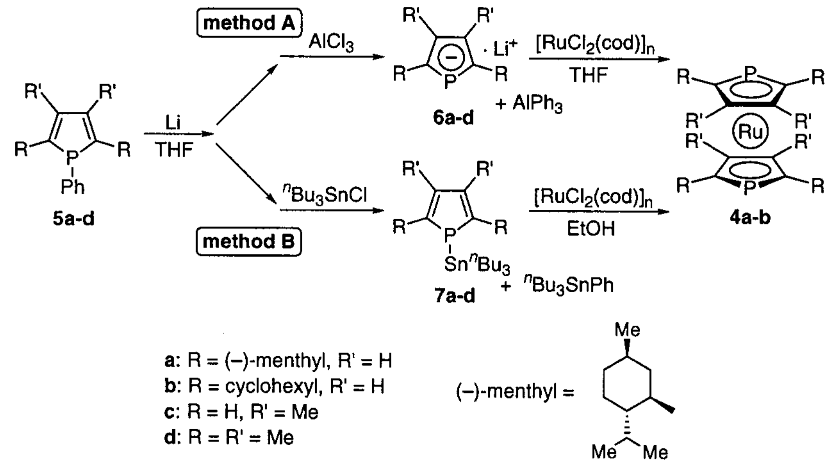
Scheme 1



separating from co-generated ^{n}Bu$_3$SnPh. Treatment of [RuCl$_2$(cod)]$_n$ with **7a** (2 equiv to Ru) in ethanol gave **4a** in 79% yield.[13] The diphospharuthenocene **4a** was isolated as a moderately air-sensitive, poorly crystalline solid by silica gel chromatography. The complex is thermally stable and further purified by sublimation under high vacuum.

The present synthetic methods of 1,1′-diphospharuthenocene are highly sensitive to steric characteristics of the phospholyl-transfer reagents **6** and **7**. While both methods afford the diphospharuthenocene **4a** in good yields, the corresponding cyclohexyl analogue **4b** was obtained in a reasonable yield only by method A. The yields of **4b** by methods A and B are 71% and 4%, respectively. Because (−)-menthyl and cyclohexyl groups possess similar electronic characteristics, the present results should be attributed to a difference in the steric nature between the two. The complex **4b** was isolated as a thermally stable pale yellow solid by silica gel chromatography followed by vacuum sublimation, and thus the low yield by method B cannot be accounted for by instability of **4b**. Attempts to prepare analogous diphospharuthenocenes using sterically more compact phospholes, such as **5c** or **5d**, were unsuccessful.[5] Apparently, steric protection of the nucleophilic phosphorus atoms in **6** and **7** was the key to success in the preparation of **4**. The present results suggest that the two (−)-menthyl groups in **6a**/**7a** are highly effective in shielding the phosphorus lone pair.

The NMR data of **4a** are consistent with coordination of the phospholyl ligand in an η^5-fashion in the complex. The C_2-symmetry of the free phospholyl, which has the chiral (−)-menthyl substituents, is broken by the η^5-coordination to the ruthenium center. Indeed, the two β-hydrogens of the η^5-phospholyl in **4a** are inequivalent to each other and give two resonances at δ 5.10 and 5.45 in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum of **4a** showed two C$_\alpha$ signals with a large $^1J_{PC}$ coupling constant at δ 110.6 (J_{PC} = 66.2 Hz) and 113.2 (J_{PC} = 67.2 Hz) as well as two C$_\beta$ signals at δ 79.9 (J_{PC} = 3.6 Hz) and 89.7 (J_{PC} = 3.6 Hz). These chemical shifts and coupling constants are comparable to those reported for the monophospharuthenocene **1**.[5]

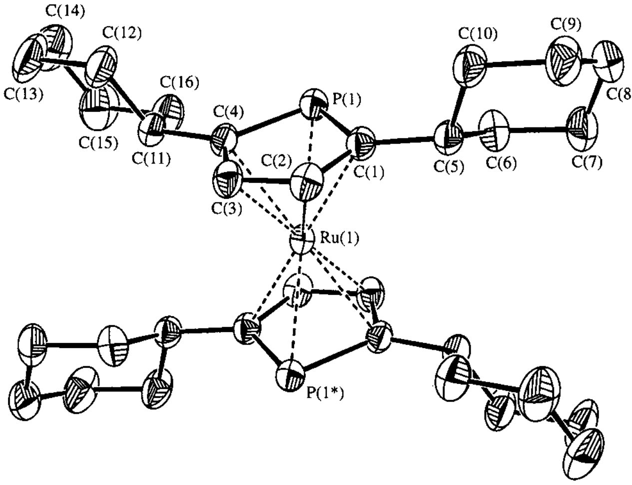


Figure 1. Figure 1. ORTEP drawing of **4b** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)−C(1) = 1.786(2), P(1)−C(4) = 1.789(2), C(1)−C(2) = 1.416(2), C(2)−C(3) = 1.424(2), C(3)−C(4) = 1.416(2), Ru(1)−phopsholyl = 1.811(2); C(1)−P(1)−C(4) = 90.37(8), P(1)−C(1)−C(2) = 111.7(1), C(1)−C(2)−C(3) = 113.2(1), C(2)−C(3)−C(4) = 113.1(1), P(1)−C(4)−C(3) = 111.6(1).

The complex **4b** was characterized by X-ray crystal structure analysis, which confirmed the η^5-coordination of the phospholyl ligand to the ruthenium center (Figure 1). For structural comparison, the homologous diphosphaferrocene Fe(η^5-2,5-Cy-phospholyl)$_2$ (**8**) was prepared and the structure was also determined by X-ray analysis (Figure 2). The complexes **4b** and **8** are nearly isostructural, and the ruthenium in **4b** and the iron in **8** are located at the center of symmetry. No intermolecular interaction was detected for both **4b** and **8**. In each complex, the two phospholyl rings are parallel and attain a staggered conformation. The nearly planar phospholyl ligands are slightly distorted, and the phosphorus atom lies out of the C(1)−C(2)−C(3)−C(4) plane by 0.035 Å in **4b** and 0.029 Å in **8** away from the central metal. The distance between a least-squares plane of the phospholyl ligand and the metal center is 1.811(2) Å in **4b** and 1.671(3) Å in **8**. The distance in **4b** is about 8% longer than that in **8**, which can be attributed to

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[12] Roberts, R. M. G.; Silver, J.; Wells, A. S. *Inorg. Chim. Acta* **1986**, *119*, 1.

[13] It was reported that a reaction of stannylcyclopentadiene with [RuCl$_2$(cod)]$_n$ in ethanol gave ruthenocene in high yield. See: (a) Liles, D. C.; Shaver, A.; Singleton, E.; Wiege, M. B. *J. Organomet. Chem.* **1985**, *288*, C33. (b) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E.; Wiege, M. B.; Boeyens, J. C. A.; Levendis, D. C. *Organometallics* **1986**, *5*, 2321.

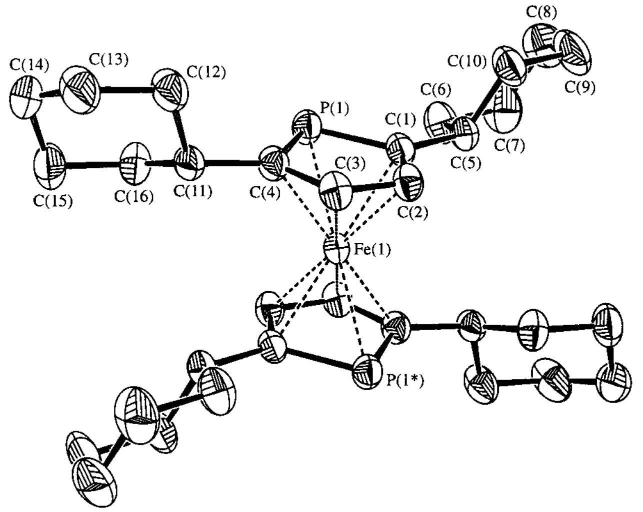
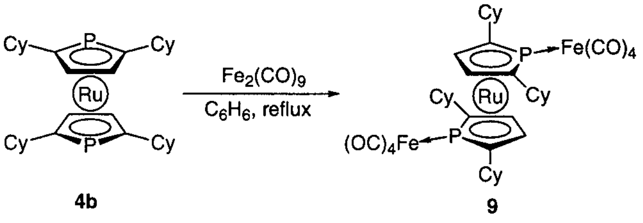


Figure 2. ORTEP drawing of **8** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)−C(1) = 1.787(2), P(1)−C(4) = 1.780(2), C(1)−C(2) = 1.410(3), C(2)−C(3) = 1.415(3), C(3)−C(4) = 1.415(3), Fe(1)−phopsholyl = 1.671(3); C(1)−P(1)−C(4) = 90.3(1), P(1)−C(1)−C(2) = 111.6(2), C(1)−C(2)−C(3) = 113.3(2), C(2)−C(3)−C(4) = 113.1(2), P(1)−C(4)−C(3) = 111.7(2).

Scheme 2



the larger atomic radius of Ru than that of Fe. The phospholyl−Fe distance in **8** is within the range of those in the other structurally characterized diphosphaferrocenes;[3b,4d,14] steric influence from the bulky cyclohexyl sidearms was hardly detected in the solid state structure of **8**. Thus, it can be deduced that the observed structure of **4b**, which is the homologue of **8**, reflects an electronic structure of an $(\eta^5\text{-}C_4P)_2Ru$ core.

As reported for phosphaferrocenes[3c,15a] and phosphacymantrenes,[15b] the diphospharuthenocenes have localized lone pairs on the phosphorus atoms. Treatment of **4b** with 2.1 equiv of $Fe_2(CO)_9$ in boiling benzene gave a bis-$Fe(CO)_4$ complex **9** in nearly quantitative yield (Scheme 2). The complex **9** showed NMR characteristics (downfield shift of the ^{31}P NMR resonance and the smaller $^1J_{CP}$ value) similar to those of the previously known phosphametallocene-*P*-$Fe(CO)_4$ species.[3c,15]

Experimental Section

General Considerations. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. Tetrahydrofuran and benzene were distilled from sodium benzophenone-ketyl under nitrogen prior to use. Ethanol was dried over magnesium, distilled, and stored in a flask with a Teflon stopcock. Phenylphosphine,[16] 1,4-dicyclohexyl-1,3-butadiyne,[17] 1-phenylphospholes (**5a**,[10] **5c**,[18] **5d**[19]), and $[RuCl_2(\eta^4\text{-}C_8H_{12})]_n$[20] were prepared as reported. ^{n}Bu$_3$SnCl was purchased from Tokyo Chemical Industry and used after appropriate purification. Lithium metal, anhydrous $AlCl_3$, and $Fe_2(CO)_9$ were purchased from Aldrich Chemical Co. and used as received. ^{n}BuLi in hexane was obtained from Kanto Chemicals. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz). ^{1}H and ^{13}C chemical shifts were referenced to the residual solvent (or the solvent) resonances and reported with respect to tetramethylsilane. ^{31}P NMR chemical shifts are externally referenced to 85% H_3PO_4. Optical rotations were measured on a JASCO DIP-370 polarimeter.

1-Phenyl-2,5-dicyclohexylphosphole (5b). A solution of *n*-butyllithium in hexane (1.59 mol/L, 17.5 mL, 27.8 mmol) was added dropwise to a solution of $PhPH_2$ (3.02 g, 27.4 mmol) in THF−C_6H_6 (80 mL, 1:1 mixture) at 0 °C. The resulting yellow solution was added dropwise to a THF (20 mL) solution of 1,4-dicyclohexyl-1,3-butadiyne (1.96 g, 9.14 mmol) by means of cannula transfer. After the addition, the wine-red mixture was heated to reflux for 2 h to give the reddish-brown suspension. This suspension was quenched with water (ca. 1.5 mL), and the mixture was evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel (elution with hexane−$CHCl_3$, 10:1) under nitrogen and then further purified by recrystallization from hot EtOH to give the analytically pure compound as colorless crystals. Yield: 1.64 g (5.05 mmol, 55%). Mp: 70.0−70.5 °C. ^{1}H NMR ($CDCl_3$): δ 1.05−1.25 (m, 10H), 1.57−1.60 (m, 2H), 1.66 (br, 4H), 1.77−1.79 (m, 4H), 2.25−2.31 (m, 2H), 6.53 (d, J_{PH} = 12.9 Hz, 2H), 7.25−7.34 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.1, 26.6, 35.1 (d, J_{PC} = 45.3 Hz), 39.9 (d, J_{PC} = 15.7 Hz), 128.4 (d, J_{PC} = 8.2 Hz), 129.3 (d, J_{PC} = 1.6 Hz), 129.9 (d, J_{PC} = 10.3 Hz), 132.1 (d, J_{PC} = 9.8 Hz), 134.2 (d, J_{PC} = 19.4 Hz), 157.9 (d, J_{PC} = 4.9 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 2.55 (s). Anal. Calcd for $C_{22}H_{29}P$: C, 81.44; H, 9.01. Found: C, 81.56; H, 8.97.

Bis[η^5-2,5-di((−)-menthyl)-1-phosphacyclopentadienyl]ruthenium(II) (4a). (a) From the Lithium Phospholide (method A). A THF (3 mL) solution of the phosphole **5a** (95.2 mg, 0.218 mmol) was treated with lithium metal (16.7 mg, 2.40 mmol), and the mixture was stirred at room temperature until disappearance of **5a** (checked by TLC). The mixture was filtered through a glass filter, and to the filtrate was added anhydrous $AlCl_3$ (10.0 mg, 0.0750 mmol) at 0 °C. After allowing to warm to room temperature, the THF solution was transferred onto a slurry of $[RuCl_2(\eta^4\text{-}C_8H_{12})]_n$ (30.5 mg, 0.109 mmol/Ru) in THF (1 mL), and the mixture was refluxed for 48 h. After cooling the mixture, all the volatiles were removed under reduced pressure. The residue was extracted with hexane. The crude product was purified by preparative TLC on silica gel (elution with hexane) under an argon atmosphere to give the title compound in pure form. Yield: 61.7 mg (75.2 mmol, 69%). Mp: 95−98 °C. ^{1}H NMR (toluene-d_8, 50 °C): δ 0.78 (d, J = 7.0 Hz, 6H), 0.80−1.09 (m, 44H), 1.25−1.33 (m, 6H), 1.57−1.82 (m, 14H), 2.09 (sept of d, J = 7.0 and 2.3 Hz, 2H), 2.17−2.19 (m, 2H), 2.31 (sept of d, J = 7.0 and 2.3 Hz, 2H), 5.09−5.10 (br, 2H), 5.44−5.46 (br, 2H). ^{13}C{^{1}H} NMR[21] (toluene-d_8, 50 °C): δ 79.9 (d, J_{PC} = 3.6 Hz), 89.7 (d, J_{PC} = 3.6 Hz), 110.6 (d, J_{PC} = 66.2 Hz), 113.2 (d, J_{PC} = 67.2 Hz). ^{31}P{^{1}H} NMR (toluene-d_8, 50 °C): δ −35.0 (s). $[\alpha]^{20}_D$ −224 (*c* 0.418, $CHCl_3$).

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[15] (a) Mathey, F. *J. Organomet. Chem.* **1978**, *154*, C13. (b) Breque, A.; Mathey, F.; Santini, C. *J. Organomet. Chem.* **1979**, *165*, 129.

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[17] Zweifel, G.; Lynd, R. A.; Murray, R. E. *Synthesis* **1977**, 52.

[18] Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.

[19] Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.

[20] Albers, M. O.; Singleton, E.; Yates, Y. E. *Inorg. Synth.* **1989**, *26*, 253.

[21] Only the data for the phospholyl ring-carbon signals are given.

Anal. Calcd for $C_{48}H_{80}P_2Ru$: C, 70.29; H, 9.83. Found: C, 70.42; H, 10.10.

(b) From the 1-Stannylphosphole (method B). A THF solution of the phosphole **5a** (105 mg, 0.240 mmol) was treated with lithium metal (16.7 mg, 2.40 mmol), and the mixture was stirred at room temperature until disappearance of **5a** (checked by TLC). The mixture was filtered through a glass filter, and to the filtrate was added tributyltin chloride (156 mg, 0.480 mmol) at 0 °C. After allowing to warm to room temperature, THF was removed under reduced pressure and the residue was dissolved in EtOH. The solution was added to $[RuCl_2(\eta^4\text{-}C_8H_{12})]_n$ (33.6 mg, 0.120 mmol/Ru), and the mixture was refluxed for 48 h. After cooling the mixture, it was evaporated to dryness under reduced pressure. The crude product was purified by preparative TLC on silica gel (elution with hexane) under an argon atmosphere to give the title compound in pure form. Yield: 78.1 mg (95.2 mmol, 79%). All the spectroscopic data are consistent with those described above.

Bis(η^5-2,5-dicyclohexyl-1-phosphacyclopentadienyl)ruthenium(II) (4b). The compound was prepared by either method A or B as described above and purified by recrystallization from hot hexane. Mp: 207−208 °C. ^{1}H NMR ($CDCl_3$): δ 1.08−1.25 (m, 20H), 1.62−1.64 (m, 4H), 1.70−1.85 (m, 20H), 5.15 (d, $J_{PH} = 4.8$ Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.21 (s), 26.80 (s), 26.87 (s), 36.37 (d, $J_{PC} = 9.8$ Hz), 37.06 (d, $J_{PC} = 4.1$ Hz), 40.24 (d, $J_{PC} = 14.0$ Hz), 80.63 (d, $J_{PC} = 4.7$ Hz), 112.49 (d, $J_{PC} = 64.7$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −46.2 (s). Anal. Calcd for $C_{32}H_{48}P_2Ru$: C, 64.52; H, 8.12. Found: C, 64.25; H, 8.05.

Bis(η^5-2,5-dicyclohexyl-1-phosphacyclopentadienyl)iron(II) (8). A THF (15 mL) solution of the phosphole **5b** (650 mg, 2.00 mmol) was treated with lithium metal (100 mg, 14.5 mmol), and the mixture was stirred at room temperature until disappearance of **5b** (checked by TLC). The mixture was filtered through a glass filter, and to the filtrate was added anhydrous $AlCl_3$ (135 mg, 0.670 mmol) at 0 °C. After allowing to warm to room temperature, the THF solution was transferred onto a slurry of anhydrous $FeCl_2$ (130 mg, 1.03 mmol) in THF (10 mL) by means of cannula. After stirring the mixture for 12 h at room temperature, all the volatiles were removed under reduced pressure. The residue was extracted with hot octane, and the extract was passed through a short pad of silica gel. Recrystallization from hot octane gave two crops of prismatic bright-red crystals. Yield: 381 mg (692 mmol, 67%). Mp: 187−188 °C. ^{1}H NMR ($CDCl_3$): δ 1.10−1.36 (m, 20H), 1.65−1.68 (m, 4H), 1.74−1.78 (m, 8H), 1.92−1.95 (m, 4H), 1.99−2.08 (m, 8H), 4.82 (d, $J_{PH} = 4.6$ Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.31 (s), 26.80 (s), 26.89 (s), 36.59 (d, $J_{PC} = 9.8$ Hz), 36.69 (d, $J_{PC} = 2.1$ Hz), 40.44 (d, $J_{PC} = 15.0$ Hz), 79.84 (d, $J_{PC} = 5.2$ Hz), 111.28 (d, $J_{PC} = 62.1$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −64.3 (s). Anal. Calcd for $C_{32}H_{48}P_2Fe$: C, 69.82; H, 8.79. Found: C, 69.80; H, 8.55.

Bis(η^5-2,5-dicyclohexyl-*P*-tetracarbonyliron(0)-1-phosphacyclopentadienyl)ruthenium(II) (9). A mixture of **4b** (60 mg, 0.10 mmol) and $Fe_2(CO)_9$ (75 mg, 0.21 mmol) was suspended in benzene (5 mL) and refluxed for 8 h. The cooled mixture was evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with deoxygenated hexane−benzene (80:20). After removal of the solvent under reduced pressure, the title complex was obtained as a yellow powder. Yield: 85 mg (90%). The complex was light-sensitive and slowly decomposed into uncharacterized species. ^{1}H NMR ($CDCl_3$): δ 1.16−1.35 (m, 20H), 1.56−1.94 (m, 24H), 5.50 (d, $J_{PH} = 16.5$ Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.85 (s), 26.77 (s), 26.95 (s), 33.91 (vt, $J_{PC} = 3.1$ Hz), 37.00 (br), 37.85 (vt, $J_{PC} = 5.7$ Hz), 80.94 (d, $J_{PC} = 4.1$ Hz), 105.13 (d, $J_{PC} = 3.6$ Hz), 214.66 (br). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.95 (s). Because of the light-sensitivity of the complex, satisfactory elemental analysis data were not obtained.

Table 1. Crystallographic Data for Complex 4b and 8

	4b	**8**
formula	$C_{32}H_{48}P_2Ru$	$C_{32}H_{48}P_2Fe$
fw	595.75	550.53
color, habit	pale yellow, prismatic	orange, prismatic
cryst size (mm)	0.35 × 0.26 × 0.11	0.10 × 0.15 × 0.20
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.821(3)	9.643(3)
b (Å)	13.428(3)	13.394(7)
c (Å)	6.146(2)	6.203(3)
α (deg)	100.83(2)	100.97(4)
β (deg)	104.87(2)	104.68(3)
γ (deg)	72.24(2)	71.66(3)
V (Å^3)	740.7(3)	730.3(6)
Z	1	1
D_{calc} (g cm^{-3})	1.335	1.252
μ (cm$^{-1)}$	6.56	6.44
F_{000}	314.00	296.00
radiation type	Mo Kα	Mo Kα
wavelength (Å)	0.71069	0.71069
T (K)	296	296
$2\theta_{max}$ (deg)	60	60
total no. of data	4558	4624
no. of unique data	4324	4295
no. of obsd data	4021 ($I > 3.00\sigma(I)$)	3031 ($I > 3.00\sigma(I)$)
no. of variables	184	184
R,[a] R_w[b]	0.024, 0.025	0.037, 0.038
gof	1.09	1.14
residual ρ (e Å$^{-3)}$	+0.67, −0.52	+0.78, −0.28

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$.

X-ray Structure Determination of 4b and 8. Suitable crystals were obtained by recrystallization from hexane (**4b**) or octane (**8**). Crystal data and other details of the structure analyses are summarized in Table 1 and the Supporting Information. Crystals of suitable size were mounted on glass fibers and then transferred to a goniostat for characterization and data collection. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SIR88 for **4b**, SIR92 for **8**) and expanded using Fourier techniques. In the final cycles of refinement, the nonhydrogen atoms were varied with anisotropic thermal parameters and the hydrogen atoms were varied with isotropic thermal parameters. All calculations were performed using the CrystalStructure[22,23] crystallographic software package.

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Supporting Information Available: Tables of crystallographic data for **4b** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] *CrystalStructure 2.00*, Crystal Structure Analysis Package; Rigaku and MSC, 2001.

[23] Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS* Issue 10; Chemical Crystallography Laboratory: Oxford, UK.