Five-Coordinate 16-Electron Carbene- and Vinylideneruthenium(II) Complexes Prepared from $[RuCl_2(C_8H_{12})]_n$ or from the New Dihydridoruthenium(IV) Compound $[RuH_2Cl_2(P^iPr_3)_2]$

Claus Grünwald, Olaf Gevert, Justin Wolf, Pablo González-Herrero,† and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland,
D-97074 Würzburg, Germany

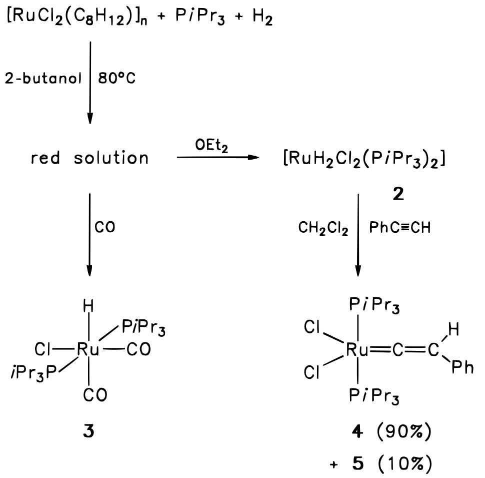
Received December 13, 1995⊗

Summary: The dihydridoruthenium(IV) compound $[RuH_2Cl_2(P^iPr_3)_2]$ (**2**), *which is obtained on treatment of* $[RuCl_2(C_8H_{12})]_n$ *with* P^iPr_3 *in 2-butanol in the presence of* H_2*, reacts with* $PhC{\equiv}CH$ *in* CH_2Cl_2 *at 25 °C to give a mixture of* $[RuCl_2({=}C{=}CHPh)(P^iPr_3)_2]$ (**4**) *and* $[RuCl_2({=}CHCH_2Ph)(P^iPr_3)_2]$ (**5**). *Both complexes* **4** *and* **5** *as well as the methylcarbene derivative* $[RuCl_2({=}CHCH_3)(P^iPr_3)_2]$ (**6**) *have been isolated; moreover, compounds* **2** *and* **5** *have been characterized by X-ray crystal structure analyses.*

After we reported the synthesis, molecular structure, and catalytic activity of the unusual 16-electron osmium(IV) compound $[OsH_2Cl_2(P^iPr_3)_2]$ (**1**),[1] it was recently found that the reaction of **1** with terminal alkynes $HC{\equiv}CR$ leads to carbyne hydrido complexes $[OsHCl_2({\equiv}CCH_2R)(P^iPr_3)_2]$ in moderate to good yields.[2] To explain the unexpected formation of carbyne ligands, an $Os({=}C{=}CHR)(\eta^2\text{-}H_2)$ species has been postulated as an intermediate which by intramolecular hydrogen transfer gives the isolated product. Since we knew from our investigations on the reactivity of the bis(phosphine) compounds $[MCl_2\{\kappa^2(P,O)\text{-}{}^iPr_2PCH_2CH_2OMe\}_2]$ and $[MCl_2\{\kappa^2(P,O)\text{-}{}^iPr_2PCH_2CO_2Me\}_2]$ (M = Ru, Os) that the ruthenium derivatives react more readily with 1-alkynes and 1-alkynols to yield the corresponding vinylidene complexes,[3] we were interested to find a synthetic route to the hitherto unknown ruthenium(IV) compound $[RuH_2Cl_2(P^iPr_3)_2]$ (**2**). We considered this to be a suitable precursor for the preparation of either six-coordinate $[RuCl_2({=}C{=}CHR)(\eta^2\text{-}H_2)(P^iPr_3)_2]$ or five-coordinate $[RuCl_2({=}C{=}CHR)(P^iPr_3)_2]$ species.

Attempts to prepare **2** from $RuCl_3{\cdot}aq$ and triisopropylphosphine in 2-propanol, i.e., on the same route which led to the formation of **1**, failed. However, by treatment of $[RuCl_2(C_8H_{12})]_n$ (C_8H_{12} = cycloocta-1,5-diene)[4] with P^iPr_3 in 2-butanol, in the presence of H_2, the desired dichloro dihydrido complex is obtained in almost quantitative yield.[5] We note that the red solution, which is initially formed, does not contain **2** as the major species since the ^{31}P NMR spectrum of this solution displays an intense resonance at 65 ppm.[6] In contrast, the ^{31}P NMR signal of **2** appears at 103.2 ppm. There is also a difference in the reactivity of the *in situ* generated species and the isolated complex **2** insofar as the initially formed solution affords $[RuHCl(CO)_2(P^iPr_3)_2]$ (**3**)[7] on treatment with CO (Scheme 1), while **2** reacts with CO to give a mixture of products.

Scheme 1



The composition of the novel ruthenium(IV) compound **2** has been confirmed by elemental analysis and an X-ray diffraction study (Figure 1).[8] The coordination geometry around the six-coordinate metal center is very similar to that of the osmium analogue **1**.[1] It can best be described as a somewhat distorted variant of a D_{4d}

---

† On leave from the Departamento de Quimica Inorgánica, Universidad de Murcia, Murcia, Spain.

⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1996.

[1] (a) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288−293. (b) Meyer, U. Dissertation, University of Würzburg, 1988.

[2] Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683−4689.

[3] (a) Werner, H.; Stark, A.; Schulz, M.; Wolf, J. *Organometallics* **1992**, *11*, 1126−1130. (b) Werner, H.; Stark, A.; Steinert, P.; Grünwald, C.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49−62. (c) Martin, M.; Gevert, O.; Werner, H. *J. Chem. Soc., Dalton Trans.*, in press.

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

[5] The preparation of **2** is as follows: A suspension of $[RuCl_2(C_8H_{12})]_n$ (220 mg, 0.79 mmol for $n = 1$) in 20 mL of 2-butanol was treated with P^iPr_3 (316 μL, 1.65 mmol) and stirred under hydrogen (1.5 bar) for 20 h at 80 °C. Upon cooling of the solution to 25 °C, the solvent was removed, and the oily residue was recrystallized from ether to give orange crystals: yield 359 mg (93%); mp 60 °C dec. Anal. Calcd for $C_{18}H_{44}Cl_2P_2Ru$: C, 43.72; H, 8.97; Ru, 20.44. Found: C, 43.41; H, 8.83; Ru, 19.85. ^1H NMR (400 MHz, CD_2Cl_2): δ 2.30 (m, 6H, $PCHCH_3$), 1.39 (dd, $J(PH) = 14.9$, $J(HH) = 7.1$ Hz, 36H, $PCHCH_3$), −12.30 (t, $J(PH) = 19.0$ Hz, 2H, RuH_2). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 103.2 (s).

[6] (a) We speculate that the dominating species could be the dihydrogen complex $[RuHCl(H_2)(P^iPr_3)_2]$,[6b] which shows a ^{31}P NMR signal in CD_2Cl_2 at 66.5 ppm. In solution, it could be in equilibrium with **2**, $[RuHCl(H_2)_2(P^iPr_3)_2]$,[6c] and dimeric hydridoruthenium compounds. (b) Burrow, T.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1995**, *34*, 2470−2472. (c) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1994**, *13*, 3800−3804.

[7] Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221−231.

0276-7333/96/2315-1960$12.00/0

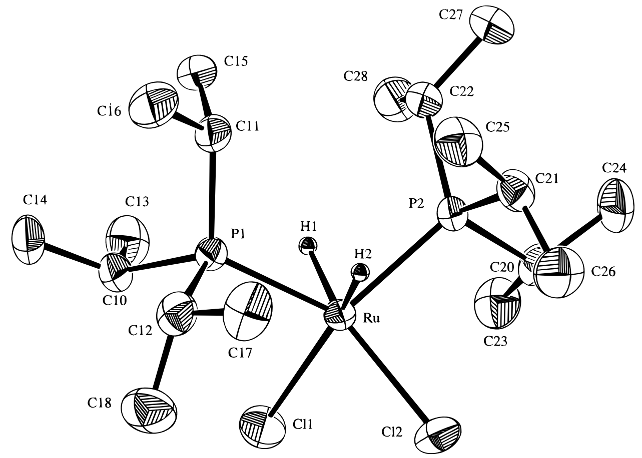
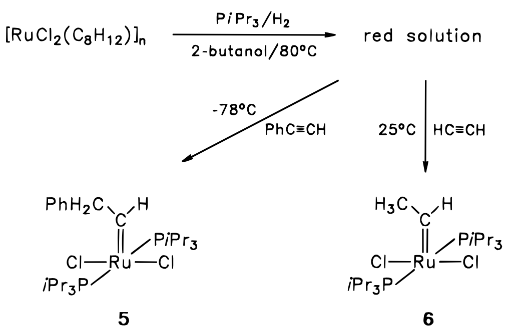


Figure 1. ORTEP diagram of compound **2** (hydrogen atoms besides H1 and H2 omitted for clarity). Selected bond distances (Å) and angles (deg): Ru−P1 2.270(1); Ru−P2 2.297(1); Ru−Cl1 2.400(1); Ru−Cl2 2.401(1); Ru−H1 1.46(5); Ru−H2 1.56(5); P1−Ru−P2 111.69(3); Cl1−Ru−Cl2 84.29(3); P1−Ru−Cl1 92.18(3); P1−Ru−Cl2 139.14(3); P2−Ru−Cl1 145.07(3); P2−Ru−Cl2 92.60(3).

square antiprism with the two vacant coordination sites in alternate positions at one square base of this polyhedron. The Ru−P and Ru−Cl distances of **2** are almost identical to the corresponding bond lengths of **1**, and this is also true for the P−Ru−P, P−Ru−Cl, and Cl−Ru−Cl bond angles. Since the positions of the hydride ligands could be located in a difference Fourier synthesis, the distances Ru−H1 and Ru−H2 had been determined as 1.46(5) and 1.56(5) Å, respectively. For other hydridoruthenium(II) and -ruthenium(IV) complexes Ru−H bond lengths were found in the range between 1.46 and 1.73 Å.[9]

Scheme 2



Compound **2** reacts with phenylacetylene in CH_2Cl_2 at room temperature to give a mixture of two products, **4** and **5**, in the molar ratio of ca. 10:1. The main component which is exclusively formed if the initially generated mixture, after removal of the solvent, is treated again with PhC≡CH has been characterized as the five-coordinate vinylidene complex $[RuCl_2(=C=CHPh)(P^iPr_3)_2]$ (**4**)[10] (Scheme 1). With regard to the spectroscopic data of **4**, the most characteristic feature is the appearance of two low-field triplets in the ^{13}C NMR spectrum at 341.1 and 109.3 ppm, which by comparison[3,11] are assigned to the α- and β-carbon atoms of the vinylidene ligand. The ^{31}P chemical shift at 29.0 ppm for **4** is similar to that observed at 27.2 ppm for the triphenylphosphine ligands in $[RuCl_2(=C=CH\textit{t}Bu)(PPh_3)_2]$.[12]

The minor component **5** of the reaction mixture obtained from **2** and PhC≡CH at 25 °C can be prepared with ca. 70% yield if the red solution (Scheme 2) is treated with 2 equiv of phenylacetylene at −78 °C. Both the elemental analysis and the NMR spectra confirm that **5** is the benzylcarbene complex $[RuCl_2(=CHCH_2Ph)(P^iPr_3)_2]$.[13] It is important to note that related compounds of general composition $[RuCl_2(=CHR)(PPh_3)_2]$ (R = alkyl, aryl, or vinyl) have recently been obtained by Grubbs et al. either on treatment of $[RuCl_2(PPh_3)_n]$ (n = 3 or 4) with 3,3-diphenylcyclopropene or with diazoalkane derivatives.[14] Ligand exchange of PPh_3 by more basic phosphines PR'_3 (R = ^{i}Pr, Cy) led to corresponding complexes $[RuCl_2(=CHR)(PR'_3)_2]$ which

---

(8) (a) Crystals were obtained from CH_2Cl_2/2-butanol. Crystal data (from 25 reflections, $2° < \theta < 22°$): monoclinic, space group $P2_1/c$ (No. 14), $a = 12.323(3)$ Å, $b = 8.590(3)$ Å, $c = 23.366(3)$ Å, $\beta = 103.31(4)°$, $V = 2407(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.364$ g cm^{-3}, μ(Mo Kα) = 0.996 mm^{-1}; crystal size 0.30 × 0.35 × 0.55 mm. Solution details: Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.709 30 Å), graphite monochromator, zirconium filter (factor 16.4), $T = 293$ K, ω/θ scan, maximum $2\theta = 50°$, 4739 reflections measured, 4200 independent, 4200 used for refinement (3801 with $I > 2\sigma(I)$); intensity data corrected for Lorentz and polarization effects; structure solved by direct methods (SHELXS-86);[8b] atomic coordinates and anisotropic thermal parameters refined by full-matrix least squares on F_o^2 (SHELXL-93);[8c] positions of all hydrogen atoms located in a difference Fourier synthesis and refined isotropically using B_{iso} values 1.5 times larger than the calculated average B_{iso} of the appending atom; $R = 0.0271$, $wR2 = 0.0614$ for all data reflections;[8d] reflection/parameter ratio 12.3; residual electron density +0.603/−0.351 e Å^{-3}. (b) Sheldrick, G. M. SHELXS-86; Universität Göttingen, Göttingen, Germany, 1986. (c) Sheldrick, G. M. SHELXL-93; Universität Göttingen, Göttingen, Germany, 1993. (d) $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o)^2 + (0.0405P)^2 + 0.473P$, where $P = (F_o^2 + 2F_c^2)/3$.

(9) (a) Pertici, P.; Vitulli, G.; Porzio, W.; Zocchi, M. *Inorg. Chim. Acta* **1979**, *37*, L521−L522. (b) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *Inorg. Chim. Acta* **1984**, *89*, 167−173. (c) Suzuki, H.; Lee, D. H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1987**, *6*, 1569−1575. (d) Jia, G.; Meek, D. W.; Gallucci, J. C. *Inorg. Chem.* **1991**, *30*, 403−410. (e) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875−1887.

(10) The preparation of **4** is as follows: A solution of **2** (142 mg, 0.29 mmol) in 7 mL of CH_2Cl_2 was treated with phenylacetylene (63 μL, 0.57 mmol) and stirred for 5 min at room temperature. After the solvent was removed, the oily residue was dissolved in 5 mL of benzene and phenylacetylene (30 μL, 0.27 mmol) was added. The reaction mixture was heated for 10 min to 80 °C, and upon being cooled to 25 °C, the solution was brought to dryness in vacuo. Recrystallization from methanol gave a brown microcrystalline solid: yield 113 mg (66%); mp 97 °C dec. Anal. Calcd for $C_{26}H_{48}Cl_2P_2Ru$: C, 52.52; H, 8.14. Found: C, 52.85; H, 7.86. IR (KBr): ν(C=C) 1600 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.12 (m, 5H, C_6H_5), 4.71 (t, J(PH) = 3.6 Hz, 1H, =C*H*Ph), 2.79 (m, 6H, PC*H*CH$_3$), 1.29 (dvt, N = 13.2, J(HH) = 6.6 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 341.11 (t, J(PC) = 15.1 Hz, Ru=C), 133.76 (t, J(PC) = 2.5 Hz, *ipso*-C of C_6H_5), 128.53, 125.59, 124.37 (all s, C_6H_5), 109.34 (t, J(PC) = 4.3 Hz, =*C*HPh), 23.66 (vt, N = 9.5 Hz, P*C*HCH$_3$), 20.11 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 29.0 (s).

(11) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197−257.

(12) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604−9610.

(13) The preparation of **5** is as follows: A suspension of $[RuCl_2(C_8H_{12})]_n$ (193 mg, 0.68 mmol for n = 1) in 30 mL of 2-butanol was treated with P^iPr_3 (520 μL, 2.72 mmol) and stirred under hydrogen (1.5 bar) for 20 h at 80 °C. Upon cooling of the mixture to −78 °C, phenylacetylene (146 μL, 1.33 mmol) was added which led to a change of color from red to brown. The reaction was warmed to room temperature, the solvent was removed in vacuo, and the oily residue was crystallized by stirring with 9 mL of methanol. Violet crystals were isolated: yield 267 mg (67%); mp 106 °C dec. Anal. Calcd for $C_{26}H_{50}Cl_2P_2Ru$: C, 52.34; H, 8.45. Found: C, 52.07; H, 8.58. ^1H NMR (400 MHz, C_6D_6): δ 19.94 (t, J(HH) = 4.8 Hz, 1H, Ru=CH), 7.33 (m, 5H, C_6H_5), 4.33 (d, J(HH) = 4.8 Hz, 2H, C*H*$_2$Ph), 2.75 (m, 6H, PC*H*CH$_3$), 1.17 (dvt, N = 13.8, J(HH) = 6.9 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 318.04 (t, J(PC) = 7.5 Hz, Ru=C), 139.01, 128.97, 128.65, 126.64 (all s, C_6H_5), 66.02 (s, *C*H$_2$Ph), 22.63 (vt, N = 9.8Hz, P*C*HCH$_3$), 19.62 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 44.7 (s).

(14) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975. (b) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem.* **1995**, *107*, 2179−2181; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041.

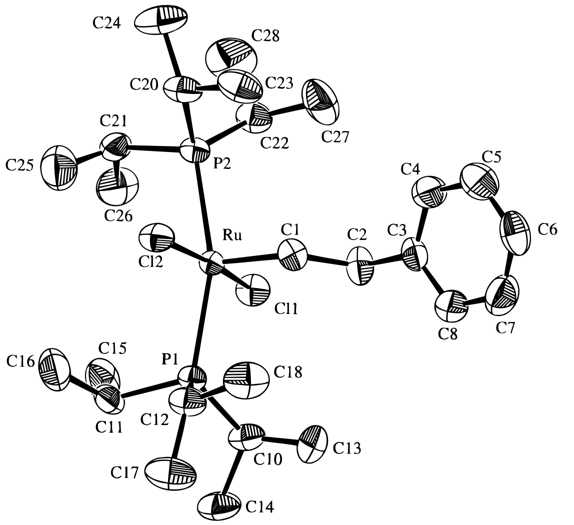


Figure 2. ORTEP diagram of compound **5** (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ru−P1 2.416(1); Ru−P2 2.423(1); Ru−Cl1 2.394(1); Ru−Cl2 2.388(1); Ru−C1 1.813(5); C1−C2 1.499(7); P1−Ru−P2 161.05(4); Cl1−Ru−Cl2 172.33(4); P1−Ru−Cl1 91.03(4); P1−Ru−Cl2 87.59(4); P1−Ru−C1 99.4(2); P2−Ru−Cl1 89.58(4); P2−Ru−Cl2 89.29(4); P2−Ru−C1 99.5(2); Cl1−Ru−C1 94.1(2); Cl2−Ru−C1 93.6(2); Ru−C1−C2 130.7(4); C1−C2−C3 112.6(4).

are highly active olefin metathesis catalysts that do not require Lewis acidic promotors.[14b,15]

The molecular structure of **5** is shown in Figure 2.[16] The ORTEP plot reveals that the geometry around ruthenium is distorted square-pyramidal. The carbene ligand is perpendicular to the Cl1−Ru−Cl2 plane with a Ru−C1 distance [1.813(5) Å] which is somewhat shorter than in the corresponding bis(tricyclohexylphosphine) complexes $[RuCl_2({=}CHCH{=}CPh_2)(PCy_3)_2]$ [1.851(21) Å][15] and $[RuCl_2({=}CHC_6H_4\text{-}p\text{-}Cl)(PCy_3)_2]$ [1.838(3) Å].[14b] The Cl1−Ru−Cl2 axis is slightly bent (172.33°), and this is even more so for the P1−Ru−P2 unit [161.05(4)°]. Although the metal center in **5** is only five-coordinate, it is nevertheless shielded quite well mainly due to the bulkiness of the six isopropyl groups. This would explain why on treatment of **5** with CO no stable 1:1 adduct is formed and styrene is eliminated instead. It should be mentioned, however, that quite recently Esteruelas, Oro, et al. reported the preparation of six-coordinate $[OsCl_2({=}CHCH_2Ph)(CO)(P^iPr_3)_2]$ which is obtained from the dihydrogen complex $[OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]$ and phenylacetylene.[17]

The methylcarbene complex $[RuCl_2({=}CHCH_3)(P^iPr_3)_2]$ (**6**) has been prepared analogously to **5** by treatment of the red solution with acetylene. Key to the structural assignment of **6** from the ^1H NMR spectrum are the quartet at 19.60 ppm for the ═CH and the doublet at 2.61 ppm for the carbene CH_3 protons.[18] The ^{13}C NMR spectrum of **6** displays a signal at 317.2 ppm which is almost identical to the position for that of **5**[13] and in the same range as those found for a variety of bis(triphenylphosphine)ruthenium(II) and -osmium(II) carbene complexes reported by Roper et al.[19]

In conclusion, we have demonstrated that both 16-electron vinylidene- and carbeneruthenium(II) compounds can be prepared from the easily available oligomeric or polymeric precusor $[RuCl_2(C_8H_{12})]_n$ and that the six-coordinate non-octahedral dichlorodihydridoruthenium(IV) complex **2** is also accessible from the same starting material. Work in progress is mainly aimed at determining the exact nature of the hydridoruthenium derivatives present in the initially formed red solution and at elucidating the mechanism of the two pathways which, by using 1-alkynes HC≡CR as substrates, led either to Ru(═C═CHR) or $Ru({=}CHCH_2R)$ derivatives.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 347), the Fonds der Chemischen Industrie, and the Dirección General de Investigación Cientifica y Técnica, Spain.

Supporting Information Available: Tables of crystallographic data, data collection, and solution and refinement details, positional and thermal parameters, and bond distances and angles for **2** and **5** (9 pages). Ordering information is given on any current masthead page.

OM9509554

---

(15) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859.

(16) Crystals were obtained from toluene. Crystal data (from 25 reflections, $2° < \theta < 20°$): triclinic, space group $P\bar{1}$ (No. 2), $a = 8.675(2)$ Å, $b = 9.721(2)$ Å, $c = 18.695(2)$ Å, $\alpha = 76.42(1)°$, $\beta = 82.14(2)°$, $\gamma = 75.19(2)°$, $V = 1475.9(7)$ Å^3, $Z = 2$, $D_{calcd} = 1.342$ g cm^{-3}, μ(Mo Kα) = 0.824 mm^{-1}; crystal size 0.55 × 0.30 × 0.25 mm. Solution details: Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.709 30 Å), graphite monochromator, zirconium filter (factor 15.4), $T = 293$ K, ω/θ scan, maximum $2\theta = 45.9°$, 4420 reflections measured, 4098 independent, 4098 used for refinement (3607 with $I > 2\sigma(I)$); intensity data corrected for Lorentz and polarization effects; structure solved by direct methods (SHELXS-86);[8b] atomic coordinates and anisotropic thermal parameters refined by full-matrix least squares on F_o^2 (SHELXL-93);[8c] positions of all hydrogen atoms calculated according to ideal geometry and used only in structure factor calculation; $R = 0.0361$, w$R2 = 0.1193$ for all data reflections;[8d] reflection/parameter ratio 14.2; residual electron density +0.390/−0.450 e Å^{-3}.

(17) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935−7942.

(18) Data for **6**: Violet crystals, mp 102 °C dec. Anal. Calcd for $C_{20}H_{46}Cl_2P_2Ru$: C, 46.15; H, 8.91. Found: C, 46.34; H, 8.87. ^1H NMR (400 MHz, C_6D_6): δ 19.60 (q, J(HH) = 5.6 Hz, 1H, Ru═CH), 2.79 (m, 6H, $PC\mathit{H}CH_3$), 2.61 (d, J(HH) = 5.6 Hz, 3H, $={}CHC\mathit{H}_3$), 1.18 (dvt, N = 13.8, J(HH) = 6.9 Hz, 36H, $PCHC\mathit{H}_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 317.18 (t, J(PC) = 7.5 Hz, Ru═C), 49.54 (s, $={}CH\mathit{C}H_3$), 22.52 (vt, N = 10.1 Hz, $P\mathit{C}HCH_3$), 19.89 (s, $PCH\mathit{C}H_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 45.35 (s).

(19) (a) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *358*, 411−447. (b) Clark, G. R.; Hodgson, D. J.; Ng, M. M. P.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1552−1554.