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On the Reaction of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ with Silylated Lithium Phosphides. Crystal and Molecular Structure of $(\eta^5\text{-}C_5Me_5)(CO)_2RuC(O)P(t\text{-}Bu)(SiMe_3)$

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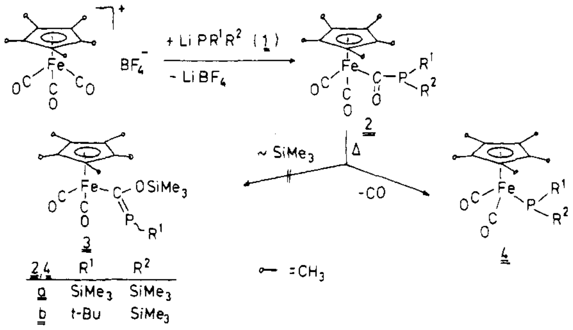
The reaction of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ with $Li[PR(SiMe_3)]$ in diethyl ether at -78 °C afforded the novel phosphinocarbonyl complexes $(\eta^5\text{-}C_5Me_5)(CO)_2RuC(O)PR(SiMe_3)$ (R = $SiMe_3$, *t*-Bu, Ph). Only the derivative with R = *t*-Bu could be isolated from the reaction mixture as yellow air-sensitive crystals. The other compounds decomposed to the phosphido complexes $(\eta^5\text{-}C_5Me_5)(CO)_2RuPR(SiMe_3)$ (R = Me_3Si, Ph) which were also synthesized by treating $(\eta^5\text{-}C_5Me_5)(CO)_2RuBr$ with $Li[PR(SiMe_3)]$. The novel coordination compounds were characterized by elemental analyses and spectroscopic methods (IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy). The molecular structure of $(\eta^5\text{-}C_5Me_5)(CO)_2RuC(O)(t\text{-}Bu)(SiMe_3)$ was established by a complete single-crystal diffraction study [$P2_1/c$ space group, $Z = 4$, $a = 16.256$ (8) Å, $b = 8.816$ (5) Å, $c = 18.016$ (7) Å, $\beta = 115.07$ (3)°].

Introduction

We recently reported the synthesis of the novel phosphinocarbonyl complexes $(\eta^5\text{-}C_5Me_5)(CO)_2FeC(O)P(R)(SiMe_3)$ (R = *t*-Bu, $SiMe_3$) by the reaction of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_3]^+BF_4^-$ with lithium phosphides[1] (eq 1). These complexes can be considered as the phosphorus analogues of the well-studied class of carbamoyl complexes.[2]



(1)

When gently heated, complexes **2a,b** did not rearrange to phosphaalkenyl complexes **3** but decarbonylated to the phosphido complexes **4**. We assumed that severe steric congestion in the coordination sphere of the hypothetical **3** might account for this observation.[3] Therefore, we extended our investigations on phosphinocarbonyl complexes as potential precursors of phosphaalkenyl complexes of metals from iron to ruthenium. Here the increased atomic radius of the metal should lower the steric interactions between the bulky ligands in a phosphaalkenyl complex such as **3**.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Perkin-Elmer Model 597 spectrometer. The ^1H and ^{31}P NMR spectra were taken on a Varian XL 200 NMR spectrometer. Spectral standards were $SiMe_4$ (^1H) and 85% H_3PO_4 (^{31}P). Chemical ionization mass spectra were recorded on a Varian MAT 312 spectrometer. Elemental analyses were performed in the Microanalytical Laboratory of the University Essen.

Materials. The lithium phosphides $Li[P(SiMe_3)_2]\cdot 2THF$,[4] $Li[P(t\text{-}Bu)(SiMe_3)]$,[5] $Li[P(Ph)(SiMe_3)]$,[5] and the complex $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ [6] were prepared as described in the literature. All solvents were rigorously dried with an appropriate drying agent and distilled prior to use.

Preparation of Compounds. $(\eta^5\text{-}C_5Me_5)(CO)_2RuBr$. A solution of 0.624 g (3.92 mmol) of bromine in 50 mL of CH_2Cl_2 was added dropwise to a solution of 2.290 g (3.92 mmol) of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2$ in 50 mL of CH_2Cl_2 (-30 °C). The yellow solution was stirred for another hour at ambient temperature. Solvent was then removed. The orange-brown residue was crystallized from a CH_2Cl_2–hexane mixture yielding 2.300 g of yellow crystalline $(\eta^5\text{-}C_5Me_5)(CO)_2RuBr$ (80%): IR (hexane) 2040 s, 1985 s cm⁻¹ (ν(CO)); ^1H NMR (C_6D_6) δ 1.45 (s, $C_5(CH_3)_5$). Anal. Calcd for $C_{12}H_{15}BrO_2Ru$ (372.2): C, 38.71; H, 4.06; Br, 21.46. Found: C, 39.00; H, 4.21; Br, 20.75.

Reaction of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+$ with $Li[P(SiMe_3)_2]\cdot 2THF$ (1a). A solution of 1.008 g (3.07 mmol) of $Li[P(SiMe_3)_2]\cdot 2THF$ in 15 mL of diethyl ether was added dropwise to a vigorously stirred ether suspension (50 mL) of 1.250 g (3.07 mmol) of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ at -78 °C. A yellow solution was formed, which was allowed to warm to ambient temperature within 30 min. Solvent was removed in vacuo, and the yellow residue was extracted with 50 mL of hexane. After filtration and concentration to 10 mL, the solution was cooled to -25 °C. After 12 h, 0.580 g (40%) of [bis(trimethylsilyl)phosphido]dicarbonyl(pentamethylcyclopentadienyl)ruthenium (**6a**) was collected by filtration. Workup of the same reaction at 0 °C again give **6a** in 59% yield: IR (Nujol) 2202 s, 1950 s (ν(CO)), 1242 s (δ (Si(CH₃)₃)), 1075 w, 1030 w, 850 s, 830 s (ρ(Si(CH₃)₃)), 748 w, 728 w, 683 m, 629 m, 589 w, 567 m, 540 w, 520 w, 469 w cm⁻¹. ^1H NMR (C_6D_6) δ 0.49 (d, $^3J_{PH}$ = 4.0 Hz, 18 H, Si(CH₃)₃), 1.53 (s,

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15 H, $C_5(CH_3)_5$); ^{13}C NMR (C_6D_6) δ 5.4 (d, $^2J_{PC}$ = 12.6 Hz, $Si(CH_3)_3$), 9.8 (d, $^3J_{PC}$ = 7.1 Hz, $C_5(CH_3)_5$), 100.4 (s, $C_5(CH_3)_5$), 204.5 (s, CO); ^{31}P NMR (C_6D_6) δ −219.9. Anal. Calcd for $C_{18}H_{33}O_2PRuSi_2$: C, 46.03; H, 7.08; mol wt, 469.7. Found: C, 45.47; H, 7.01; mol wt, 469 (MS/CI).

Reaction of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ with LiP(*t*-Bu)($SiMe_3$) (1b). The reaction of 1.550 g (3.81 mmol) of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ with 3.81 mmol of **1b** (20 mL of a 0.19 M solution in ether) was formed analogously to give 0.950 g (52%) of yellow, air-sensitive [(*tert*-butyl(trimethylsilyl)phosphino)carbonyl]dicarbonyl(pentamethylcyclopentadienyl)ruthenium (**5b**): IR (Nujol) 2010 s, 2005 sh, 1955 s, 1947 s ($\nu(CO)_{term}$), 1618 m ($\nu(CO)_{acyl}$), 1360 sh, 1245 w, ($\delta(Si(CH_3)_3)$), 1172 w, 1075 w, 1030 w, 842 m ($\rho(Si(CH_3)_3)$), 757 m, 730 m, 692 w, 632 w, 588 w, 545 w, 508 w, 475 w cm^{-1}; ^1H NMR (C_6D_6) δ 0.43 (d, $^3J_{PH}$ = 2.9 Hz, 9 H, $Si(CH_3)_3$), 1.37 (d, $^3J_{PH}$ = 10.7 Hz, 9 H, $t\text{-}C_4H_9$), 1.58 (s, 15 H, $C_5(CH_3)_5$); ^{13}C NMR (C_6D_6) δ = 2.5 (d, $^2J_{PC}$ = 7.3 Hz, $Si(CH_3)_3$), 9.6 (s, $C_5(CH_3)_5$), 31.2 (d, $^2J_{PC}$ = 10.8 Hz, $C(CH_3)_3$), 36.0 (d, $^1J_{PC}$ = 29.3 Hz, $C(CH_3)_3$), 100.8 (s, $C_5(CH_3)_5$), 203.5 (s, br, $(CO)_{term}$), 259.0 (d, $^1J_{PC}$ = 112.8 Hz, $(CO)_{acyl}$); ^{31}P NMR (C_6D_6) δ 67.4 s; MS/EI (70 eV, 70 °C), *m/e* 481 (M^+), 453 (M^+ − CO), 425 (M^+ − 2CO), 396 (M^+ − 3CO, −H), 320 $[(C_5Me_5)Ru(CO)_3^+]$, 292 $[(C_5Me_5)Ru(CO)_2^+]$, 264 $[(C_5Me_5)Ru(CO)^+]$, 236 $[(C_5Me_5)Ru^+]$, 73 ($SiMe_3^+$), 57 ($t\text{-}C_4H_9^+$). Anal. Calcd for $C_{20}H_{33}O_3PRuSi$ (481.6): C, 49.88; H, 6.91. Found: C, 49.98, H, 7.21.

Reaction of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ with Li[P(Ph)$SiMe_3$] (1c). Analogously, 1.02 g (2.51 mmol) of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ and 2.51 mmol of **1c** (15 mL of a 0.167 M solution in ether) were allowed to react yielding 0.630 g (53%) of yellow, air-sensitive [phenyl(trimethylsilyl)phosphido]dicarbonyl(pentamethylcyclopentadienyl)ruthenium (**6c**): IR (Nujol) 3040 w, 2000 s, 1948 s (ν(CO)), 1578 w, 1430 w, 1242 m ($\delta(Si(CH_3)_3)$), 1070 w, 1035 sh, 1028 m, 835 s ($\rho(Si(CH_3)_3)$), 740 m, 700 m, 633 w, 588 w, 569 m, 544 w, 525 w, 515 w, 488 w, 440 w, 412 w cm^{-1}; ^1H NMR (C_6D_6) δ 0.42 (d, $^3J_{PH}$ = 4.2 Hz, 9 H, $Si(CH_3)_3$), 1.49 (s, 15 H, $C_5(CH_3)_5$), 7.08–7.92 (m, 5 H, Ph); ^{13}C NMR (C_6D_6) δ 2.0 (d, $^2J_{PC}$ = 12.0 Hz, $Si(CH_3)_3$), 9.5 (d, $^3J_{PC}$ = 4.7 Hz, $C_5(CH_3)_5$), 100.6 (s, $C_5(CH_3)_5$), 126.3–143.5 (Ph), 204.6 (s, CO); ^{31}P NMR (C_6D_6) δ −77.4. Anal. Calcd for $C_{21}H_{29}O_2PRuSi$: C, 53.26; H, 6.17; mol wt, 473.6. Found: C, 53.33; H, 6.17; mol wt, 473 (MS/CI).

Reaction of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ with 1a–c in the ^{31}P NMR Experiment at Variable Temperature. To an equimolar amount of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ was added a solution of 1 in ether at −196 °C. Warming up to −78 °C afforded a yellow solution, the ^{31}P NMR spectra of which were registered at −80, −60, −40, −20, 0, and 22 °C. $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$ (1): (a) 0.097 g (0.238 mmol), 2.50 mL of a 0.095 M solution of **1a** in ether (0.238 mmol); (b) 0.122 g (0.300 mmol), 3.44 mL of a 0.087 M solution of **1b** in ether (0.300 mmol); (c) 0.126 g (0.310 mmol), 3.26 mL of a 0.095 M solution of **1c** in ether (0.310 mmol)

Reaction of $(\eta^5\text{-}C_5Me_5)(CO)_2RuBr$ with $Li[P(SiMe_3)_2]\cdot2THF$ (1a). A solution of 1.176 g (3.58 mmol) of **1a** in 20 mL of ether was added dropwise to a slurry of 1.330 g (3.57 mmol) of $(\eta^5\text{-}C_5Me_5)(CO)_2RuBr$ in 50 mL of hexane at −30 °C. The yellow solution was warmed to room temperature, and stirring was continued for another 30 min. Solvent was removed in vacuo, and the yellow residue was extracted with 50 mL of hexane. After filtration and concentration to 10 mL, the solution was cooled to −25 °C. After 12 h, 1.060 g (63%) of **6a** was collected by filtration.

Reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2RuBr$ with Li[P(*t*-Bu)($SiMe_3$)] (1b). Analogously, 0.680 g (55%) of yellow, air-sensitive [*tert*-butyl(trimethylsilyl)phosphido]dicarbonyl(pentamethylcyclopentadienyl)ruthenium **6b**) was prepared from 1.013 g (2.72 mmol) of $(\eta^5\text{-}C_5Me_5)(CO)_2RuBr$ and 2.72 mmol of **1b** (15 mL of a 0.181 M solution in ether): IR (Nujol) 1998 s, 1945 s (ν(CO)), 1360 w, 1242 m ($\delta(Si(CH_3)_3)$, 1170 w, 1073 w, 1028 m, 840 s ($\rho(Si(CH_3)_3)$, 745 w, 738 w, 698 w, 632 w, 600 w, 570 m, 540 w, 525 w, 512 w, 500 w; ^1H NMR (C_6D_6) δ 0.51 (d, $^3J_{PH}$ = 3.8 Hz, 9 H, $Si(CH_3)_3$), 1.46 (d, $^3J_{PH}$ = 11.6 Hz, 9 H, $t\text{-}C_4H_9$), 1.55 (s, 15 H, $C_5(CH_3)_5$; ^{13}C NMR (C_6D_6) δ 4.8 (d, $^2J_{PC}$ = 11.2 Hz, $Si(CH_3)_3$), 9.8 (d, $^3J_{PC}$ = 7.1 Hz, $C_5(CH_3)_3$), 32.1 (d, $^1J_{PC}$ = 31.1 Hz, $C(CH_3)_3$), 35.4 (d, $^2J_{PC}$ = 14.2 Hz, $C(CH_3)_3$), 100.7 (s, $C_5(CH_3)_5$), 205.5 (s, CO); ^{31}P NMR (C_6D_6) δ −15.2. Anal. Calcd for $C_{19}H_{33}O_2PRuSi$ (453.6): C, 50.31; H, 7.33. Found: C, 49.88; H, 7.44; mol wt, 453 (MS/CI).

Table I. Crystallographic Data for the X-ray Diffraction Study of $(\eta^5\text{-}C_5Me_5)(CO)_2RuC(O)P(t\text{-}Bu)(SiMe_3)$ (5b)

Crystal Parameters	
cryst system	monoclinic
space group	$P2_1/c$
a, Å	16.256 (8)
b, Å	8.816 (5)
c, Å	18.016 (7)
β, deg	115.07 (3)°
V, Å^3	2339 (2)
Z	4
δ(calcd), g/cm^3	1.37
abs coeff, μ, cm^{-1}	7.89
T, °C	−125
Measurement of Intensity Data	
diffractometer	Syntex R 3 four cycle diffractometer
radiation	Mo Kα (λ = 0.71069 Å)
monochromator	graphite cyrstal
scan type	2θ:ω
scan speed	variable 2–30°/min
scan width	0.8°
data limits	3° ≤ 2θ ≤ 55°
unique reflns	4053
obs. reflns (*F* ≥ 3.5σ(*F*))	3694
R(merge)	0.022
R	0.040
R_w	0.043
w^{-1}	$\sigma^2(F) + 0.00045F^2$

Reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2RuBr$ with $Li[P(Ph)(SiMe_3)]$ (1c). Analogously, the reaction of 1.233 g (3.31 mmol) of $(\eta^5\text{-}C_5Me_5)(CO)_2RuBr$ with 3.31 mmol of **1c** (20 mL of a 0.166 M solution in ether) gave 0.850 g (54%) of **6c**.

X-ray Structure Determination of $[(\eta^5\text{-}C_5Me_5)RuC(O)P(t\text{-}Bu)(SiMe_3)$ (5b). Yellow crystals of **5b** were grown from a saturated hexane solution. An irregularly shaped crystal of dimensions 0.43 mm × 0.29 mm × 0.15 mm was fixed under a nitrogen atmosphere into a capillary and mounted onto the diffractometer. In order to avoid decomposition, the sample was cooled with a Nicolet LT-2 low-temperature device to −125 °C ± 0.4 °C. Table I gives the pertinent crystal and intensity data. No significant drop of intensity was observed with the reference reflections, taken every 100 reflections, measured. The structure was solved by locating the Ru atom from a Patterson map, using SHELXTL software on a Data General NOVA 3/12. A difference map phased on the heavy atom revealed the locations of all non-hydrogen atoms. The methyl hydrogen atoms were refined as rigid groups (C–H distance = 0.96 Å; H–C–H angle = 109.5°), given the 1.2-fold isotropic *U* value of the orthogonalized U_{ij} tensor of the corresponding C atom. The cyclopentadienyl ring was treated as a rigid group (C–C distance = 1.42 Å; C–C–C angle = 108.0°). In the last refinement cycle 259 parameters, including the overall scale factor, were varied, all non-hydrogen atoms given anisotropical thermal parameters; the maximum shift per error was 0.01. A final difference map showed the largest peak to be 1.05 Å^3 located 0.88 Å away from Ru. Final positional and thermal parameters are listed in Table II, relevant bond distances and angles are given in Table III, and tables in the supplementary material give the derived position of the hydrogen atom coordinates and isotropic thermal parameters and the structure factors.

Results and Discussion

By analogy to eq 1, tricarbonyl(pentamethylcyclopentadienyl)ruthenium tetrafluoroborate reacted with the lithium phosphides $Li[P(SiMe_3)_2]\cdot2THF$ (**1a**), Li[P(*t*-Bu)($SiMe_3$)] (**1b**), and Li[P(Ph)($SiMe_3$)] (**1c**) in ether at −78 °C to give the ruthenium phosphinocarbonyl complexes **5a–c**.

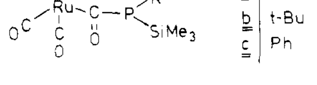


Table II. Atomic Coordinates and Anisotropical Temperature Parameters for 5b

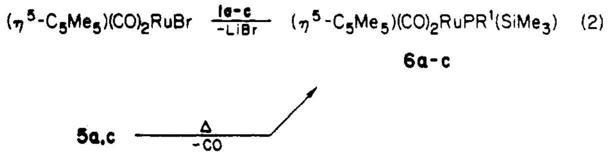
atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	0.1866 (1)	0.6521 (1)	0.7340 (1)	0.021 (1)	0.027 (1)	0.011 (1)	0.000 (1)	0.005 (1)	0.002 (1)
P(1)	0.3463 (1)	0.4291 (1)	0.8878 (1)	0.022 (1)	0.028 (1)	0.014 (1)	0.001 (1)	0.007 (1)	0.001 (1)
Si(1)	0.4143 (1)	0.3184 (1)	0.8176 (1)	0.025 (1)	0.040 (1)	0.022 (1)	−0.003 (1)	0.012 (1)	0.003 (1)
O(1)	0.1658 (2)	0.3518 (3)	0.7890 (2)	0.027 (1)	0.044 (2)	0.025 (1)	0.008 (1)	0.007 (1)	−0.002 (1)
O(2)	0.3764 (2)	0.7987 (4)	0.8047 (2)	0.032 (1)	0.046 (2)	0.047 (2)	0.008 (1)	−0.002 (1)	−0.009 (1)
O(3)	0.1615 (3)	0.7466 (4)	0.8799 (2)	0.096 (3)	0.080 (2)	0.028 (2)	0.000 (2)	0.035 (2)	0.036 (2)
C(1)	0.2241 (2)	0.4471 (4)	0.8000 (2)	0.021 (2)	0.032 (2)	0.015 (1)	−0.002 (1)	0.009 (1)	−0.001 (1)
C(2)	0.3078 (2)	0.7334 (4)	0.7821 (2)	0.030 (2)	0.034 (2)	0.019 (2)	0.005 (1)	0.001 (1)	−0.000 (1)
C(3)	0.1720 (3)	0.7117 (5)	0.8248 (2)	0.039 (2)	0.043 (2)	0.025 (2)	0.007 (2)	0.007 (2)	0.019 (2)
C(4)	0.4470 (3)	0.4686 (5)	0.7645 (3)	0.041 (2)	0.064 (3)	0.034 (2)	−0.002 (2)	0.026 (2)	−0.005 (2)
C(5)	0.5241 (3)	0.2212 (6)	0.8914 (3)	0.038 (2)	0.072 (3)	0.036 (2)	−0.003 (2)	0.014 (2)	0.022 (2)
C(6)	0.3358 (3)	0.1819 (5)	0.7383 (2)	0.046 (2)	0.041 (2)	0.028 (2)	−0.009 (2)	0.015 (2)	0.003 (2)
C(7)	0.3374 (2)	0.2741 (4)	0.9555 (2)	0.027 (2)	0.035 (2)	0.016 (2)	0.006 (1)	0.008 (1)	0.000 (1)
C(8)	0.2677 (3)	0.3359 (5)	0.9831 (2)	0.045 (2)	0.053 (2)	0.025 (2)	0.005 (2)	0.022 (2)	−0.000 (2)
C(9)	0.4328 (3)	0.2651 (5)	1.0316 (2)	0.042 (2)	0.052 (2)	0.020 (2)	0.010 (2)	0.005 (2)	0.001 (2)
C(10)	0.3079 (3)	0.1156 (4)	0.9175 (2)	0.037 (2)	0.038 (2)	0.029 (2)	0.006 (2)	0.013 (2)	−0.000 (2)
C(11)	0.0353 (1)	0.6300 (3)	0.6374 (1)	0.025 (2)	0.036 (2)	0.014 (2)	0.000 (1)	0.003 (1)	−0.002 (1)
C(12)	0.0901 (0)	0.5293 (0)	0.6162 (0)	0.028 (2)	0.034 (2)	0.013 (1)	0.003 (1)	−0.001 (1)	0.002 (1)
C(13)	0.1540 (0)	0.6173 (0)	0.6002 (0)	0.028 (2)	0.047 (2)	0.011 (2)	−0.001 (1)	0.006 (1)	0.004 (2)
C(14)	0.1386 (0)	0.7724 (0)	0.6115 (0)	0.030 (2)	0.040 (2)	0.013 (2)	0.004 (1)	0.004 (1)	−0.004 (2)
C(15)	0.0652 (0)	0.7803 (0)	0.6345 (0)	0.026 (2)	0.034 (2)	0.012 (1)	0.003 (1)	0.000 (1)	0.005 (1)
C(16)	−0.0415 (3)	0.5838 (6)	0.6548 (3)	0.029 (2)	0.068 (3)	0.035 (2)	0.005 (2)	0.012 (2)	−0.005 (2)
C(17)	0.0732 (3)	0.3595 (4)	0.6021 (3)	0.049 (3)	0.035 (2)	0.026 (2)	−0.006 (2)	−0.001 (2)	−0.003 (2)
C(18)	0.2180 (3)	0.5614 (6)	0.5695 (2)	0.052 (3)	0.081 (3)	0.024 (2)	−0.001 (2)	0.021 (2)	0.014 (2)
C(19)	0.1818(3)	0.9077 (5)	0.5925 (3)	0.054 (3)	0.052 (3)	0.032 (2)	0.011 (2)	0.011 (2)	−0.018 (2)
C(20)	0.0211 (3)	0.9239 (5)	0.6444 (3)	0.052 (3)	0.043 (2)	0.033 (2)	0.002 (2)	0.005 (2)	0.016 (2)

[a] Anisotropic temperature factors defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}a^*b^*hk + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for 5b

	Bond Lengths		
Ru(1)–C(1)	2.107 (3)	Ru(1)–C(2)	1.924 (3)
Ru(1)–C(3)	1.827 (5)	Ru(1)–C(11)	2.343 (2)
Ru(1)–C(12)	2.305 (2)	Ru(1)–C(13)	2.259 (3)
Ru(1)–C(14)	2.268 (2)	Ru(1)–C(15)	2.321 (2)
P(1)–Si(1)	2.226 (2)	P(1)–C(1)	1.952 (3)
P(1)–C(7)	1.878 (4)	Si(1)–C(4)	1.839 (5)
Si(1)–C(5)	1.917 (4)	Si(1)–C(6)	1.891 (4)
O(1)–C(1)	1.219 (4)	O(2)–C(2)	1.164 (5)
O(3)–C(3)	1.120 (6)	C(7)–C(8)	1.519 (7)
C(7)–C(9)	1.577 (4)	C(7)–C(10)	1.540 (5)
	Bond Angles		
C(1)–Ru(1)–C(2)	93.9 (1)	C(1)–Ru(1)–C(3)	81.8 (2)
C(2)–Ru(1)–C(3)	89.2 (2)	C(1)–Ru(1)–C(11)	108.1 (1)
C(2)–Ru(1)–C(11)	156.7 (1)	C(3)–Ru(1)–C(11)	101.3 (1)
C(1)–Ru(1)–C(12)	92.2 (1)	C(2)–Ru(1)–C(12)	139.2 (1)
C(3)–Ru(1)–C(12)	131.6 (1)	C(1)–Ru(1)–C(13)	111.5 (1)
C(2)–Ru(1)–C(13)	105.3 (1)	C(3)–Ru(1)–C(13)	159.0 (1)
C(1)–Ru(1)–C(14)	148.0 (1)	C(2)–Ru(1)–C(14)	97.4 (1)
C(3)–Ru(1)–C(14)	128.0 (1)	C(1)–Ru(1)–C(15)	143.3 (1)
C(2)–Ru(1)–C(15)	122.7 (1)	C(3)–Ru(1)–C(15)	99.3 (1)
Si(1)–P(1)–C(1)	98.9 (1)	Si(1)–P(1)–C(7)	104.1 (1)
C(1)–P(1)–C(7)	104.7 (1)	P(1)–Si(1)–C(4)	107.6 (2)
P(1)–Si(1)–C(5)	110.0 (2)	P(1)–Si(1)–C(6)	111.7 (2)
Ru(1)–C(1)–P(1)	118.6 (2)	Ru(1)–C(1)–O(1)	118.7 (2)
P(1)–C(1)–O(1)	122.0 (2)	Ru(1)–C(2)–O(2)	171.2 (3
Ru(1)–C(3)–O(3)	178.6 (4)	P(1)–C(7)–C(8)	103.0 (2)
P(1)–C(7)–C(9)	106.4 (3)	P(1)–C(7)–C(10)	117.8 (3)
Ru(1)–C(11)–C(12)	70.8 (1)	Ru(1)–C(11)–C(15)	71.4 (1)
Ru(1)–C(11)–C(16)	125.8 (2)	Ru(1)–C(12)–C(11)	73.7 (1)
Ru(1)–C(12)–C(13)	70.1 (1)	Ru(1)–C(12)–C(17)	128.3 (2)
Ru(1)–C(13)–C(12)	73.7 (1)	Ru(1)–C(13)–C(14)	72.1 (1)
Ru(1)–C(13)–C(18)	124.7 (2)	Ru(1)–C(14)–C(13)	71.3 (1)
Ru(1)–C(14)–C(15)	74.0 (1)	Ru(1)–C(14)–C(19)	126.5 (2)
Ru(1)–C(15)–C(11)	73.1 (1)	Ru(1)–C(15)–C(14)	70.0 (1)
Ru(1)–C(15)–C(20)	127.6 (2)		

Only compound **5b** could be isolated from the yellow reaction mixture as a yellow, crystalline, air-sensitive solid. Compounds **5a** and **5c** decomposed during workup to the ruthenium phosphido complexes **6a,c**, which were isolated in ca. 50–60% yields. The phosphido complexes **6a–c** were also synthesized independently from (η^5-C_5Me_5)$(CO)_2$RuBr and **1a–c** according to a general procedure of Schäfer[7] (eq 2).



$$(\eta^5\text{-}C_5Me_5)(CO)_2RuBr \xrightarrow[-LiBr]{1a-c} (\eta^5\text{-}C_5Me_5)(CO)_2RuPR^1(SiMe_3) \quad (2)$$

Another complex of this type, (η^5-C_5Me_5)$(CO)_2$RuP(*t*-Bu)Cl, was obtained by Malisch from K[(η^5-C_5Me_5)Ru$(CO)_2$] and Cl_2P-*t*-Bu.[8] In order to obtain a better understanding of the generation and the chemical behavior of complexes such as **5**, the reaction of [(η^5-C_5Me_5)Ru$(CO)_3$]$^+BF_4^-$ with **1a–c** was monitored by ^{31}P NMR spectroscopy. When the cation was treated with **1a** in an NMR tube at −78 °C an intense singlet was observed at δ −6.8 which was assigned to **5a** by comparison with the iron analogue **2a** ($\delta(^{31}P)$ +6.2 ppm). At 0 °C the resonance was shifted to δ −3.8, and warming up to 22 °C gave rise to an additional singlet at δ +175.4. Maintaining these conditions for another 6 h caused the appearance of a resonance at δ −219.4 for **6a**, which increased in intensity at the expense of **5a**. Now the low field area of the spectrum is dominated by two singlets at δ +175.4 and 201.5, the origin of which is unclear.

Attempted isolation of these materials failed.

By analogy, an etheral mixture of [(η^5-C_5Me_5)Ru$(CO)_3$]$^+BF_4^-$ and **1b** at −78 °C displayed a singlet at δ +67.3, readily attributed to **5b**. At 22 °C another singlet was observed at δ 271.1, and heating for 5 h at 35 °C caused an additional singlet at δ +196.6. There was no evidence for the phosphido complex **6b**. Reaction of **1c** with [(η^5-C_5Me_5)Ru$(CO)_3$]$^+BF_4^-$ at −78 °C initially gave the phosphinocarbonyl complex **5c** as evidenced by the appearance of a ^{31}P resonance at δ 33.3. However, upon warming up to −40 °C decomposition occurred to give the phosphido complex **6c** (δ −79.3). The intensity of this singlet rapidly increased when the mixture reached am-

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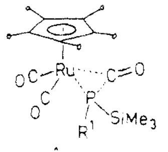
[7] Schäfer, H. *Z. Anorg. Allg. Chem.* 1981, *467*, 105.

[8] Stasunik, A.; Wilson, D. R.; Malisch, W. *J. Organomet. Chem.* 1984, *270*, C18.

bient temperature. At this temperature additional signals showed up at δ 67.6, 129.2, 153.4, and 61.9, the origin of which is unclear. Keeping the sample 5 h at 35 °C led to the complete absence of **5c** and the resonances at δ −77.1 (**6c**), 129.9, and 153.4 remained as the most intense ones. No phosphaalkenyl complexes could be isolated from all these reactions.

It is assumed that the observed stability of **5a** in solution is due to the dipolar solvent ether and the presence of $LiBF_4$. Attempted extraction of the product from the reaction residue into hexane could then account for the decomposition process **5** → **6**. Presumably, the increased size of the ruthenium in comparison to iron allows a transition state such as A from which the phosphido complex is easily formed by loss of CO.



A

Evidently only the most bulky phosphinocarbonyl ligand (*t*-Bu)(Me_3Si)PC(O) does not undergo a η^2-arrangement as in A for steric reasons, thus stabilizing compound **5b**. The constitution and configurations of **5b** and the phosphido complexes **6a–c** were deduced from elemental analysis and spectroscopic data. The molecular structure of **5b** was elucidated by X-ray analysis, whereas the characterization of **5a** and **5c** is limited to ^{31}P NMR and IR evidence. The IR spectrum of **5b** (in hexane) shows four strong metal carbonyl stretching modes at 2018, 2010, 1958, and 1950 cm^{-1}. The splitting of the symmetric and antisymmetric mode by 8 cm^{-1} could be explained by the presence of at least two conformers of **5b** in solution. The same was true for **5a**, where the ν(CO) bands registered at 2020, 2012, 1962, and 1954 cm^{-1}. A band of medium intensity at 1618 cm^{-1} in both spectra was assigned to the CO stretching vibration of the phosphinocarbonyl fragment.

Clearly, the phosphido ligands in the corresponding complexes **6a,b** [ν(CO) 2010, 1953 and 2004, 1946 cm^{-1} (in hexane), respectively] are more powerful donors than the phosphinocarbonyl ligands, which is obvious from the bathochromic shifts of 5–10 cm^{-1}. The donor capacity of the phosphido ligands increases in the series $PPh(SiMe_3) \simeq P(SiMe_3)_2 < P(t\text{-}Bu)(SiMe_3)$ [**6c**, ν(CO) 2010, 1950 cm^{-1} (in hexane)]. In the ^1H NMR experiment compounds **5b**, **6b**, and **6c** are characterized by three different signal groups whereas **6a** exhibits two resonances. The $(CH_3)_5C_5$ protons give rise to singlets in the range 1.49–1.58 ppm.

Coupling with the phosphorus accounts for the appearance of doublets for the trimethylsilyl and *tert*-butyl protons [δ 0.42–0.49 ($^3J_{PH}$ = 2.9–4.2 Hz) and δ 1.37–1.46 ($^3J_{PH}$ = 10.7 − 11.6 Hz), respectively]. In the ^{13}C NMR spectrum of **5b** the acylic carbonyl group gives rise to a doublet at δ 259 ($^1J_{PC}$ = 112.8 Hz), whereas the CO ligands are observed as a broad and poorly resolved signal at δ 203.5. These data correlate well with the corresponding chemical shifts of [$(\eta^5\text{-}C_5Me_5)(CO)_2FeC(O)P(t\text{-}Bu)(SiMe_3)$] [δ 272.2 (d, $^1J_{PC}$ = 102.2 Hz) and 217.2 (s)].[1]

The shielding of 13.7 ppm for the terminal CO's and 13.2 ppm for the acylic CO groups in going from iron to ruthenium is quite usual and a reflection of the nature of the transition metal.[9] The terminal carbonyl groups in **6a–c** are found at about the same chemical shift as in **5b** (δ(^{13}C) 204.5–205.5). The ^{31}P NMR spectrum of **5b** shows a singlet at δ 67.4 (C_6D_6).

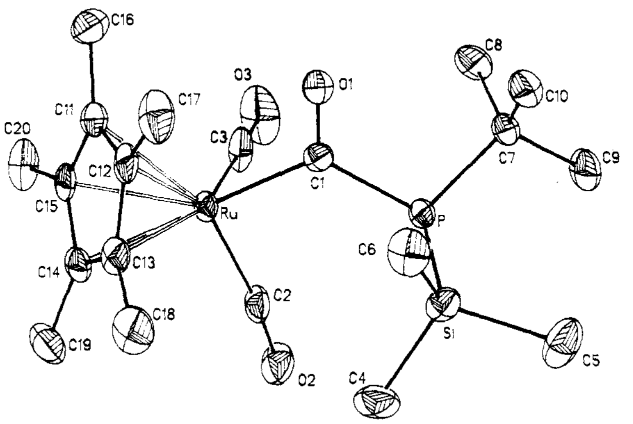


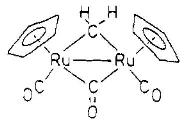
Figure 1. Molecular structure of **5b**.

Evidence is given by the ^{31}P NMR chemical shift of **5a** [δ −3.8 (ether)] and **5c** [δ 33.3 (ether)] that the replacement of a Me_3Si group by a *tert*-butyl unit leads to a deshielding of 71.1 ppm, whereas the substitution of a Me_3Si group by phenyl accounts for a low-field shift of only 37.1 ppm. These observations are consistent with the conclusions reported recently for the iron complexes **2a** and **2b** [$\Delta\delta(^{31}P)$ = 68.9 ppm].

The ^{31}P NMR nuclei of the compounds **6a–c** absorb at significantly higher fields [$\delta(^{31}P)$ −219.9 (**6a**), −15.2 (**6b**), and −77.4 (**6c**) (C_6D_6)]. Again the replacement of a silyl group in **6a** by *tert*-butyl or phenyl group results in a drastic deshielding of the ^{31}P NMR resonances (Δδ = 204.7 and 142.5 ppm).

Crystal and Molecular Structure of (η^5-C_5Me_5)$(CO)_2$RuC(O)P(*t*-Bu)($SiMe_3$) (5b)

The crystal and molecular structure of **5b** was determined by X-ray diffraction methods. The molecular geometry and atomic numbering scheme are shown in Figure 1, and the results are summarized in Tables II and III. The analysis clearly confirmed that **5b** contained a [C(O)P(*t*-Bu)($SiMe_3$)] unit linked to the metal through a Ru–C covalent bond. The ligand could be considered as one leg in a distorted three-legged piano-stool arrangement. The distortion is evidenced by two relatively short ruthenium–ring carbon distances of 2.259 (3) and 2.268 (2) Å and three significantly longer bond lengths ranging from 2.305 (2) to 2.343 (2) Å. These three ring carbon atoms (C(11), C(12), C(15)) are presumably pushed aside by the bulky phosphinocarbonyl ligand located on the same side of the molecule. As a whole the metal–ring separations in **5b** are longer than those in $Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta^5\text{-}C_5H_5)_2$[10] (**7**) (2.219 (8)–2.290 (6) Å) or in $(\eta^5\text{-}C_5H_5)(CO)_2RuC(O)NH_2$ (**8**) (2.230 (8)–2.268 (9) Å.[11]



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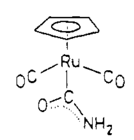

8

Two legs of the piano stool are represented by terminal carbonyl ligands with Ru–C(CO) distances of 1.827 (5) and

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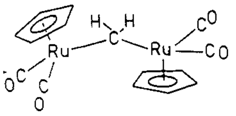
[9] (a) Braterman, P. S.; Milne, D. W.; Randal, E.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* **1973**, 1027. (b) Cotton, F. A.; Hunter, D. L.; Lahuerta, P. *J. Am. Chem. Soc.* **1974**, *96*, 7926.

[10] Davies, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2293.

[11] Wagner, H.; Jungbauer, A.; Thiele, G.; Behrens, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1979**, *B34*, 1487.

1.924 (3) Å, which differ significantly from those in **8** (1.870 (8) and 1.867 (8) Å). One of the CO ligands deviates from linearity (171.2 (3)°), whereas the second one is essentially linear 178.6 (4)°). The angle between the metal and the two CO groups is 89.2 (2)°. The most interesting structural feature of **5b** is the geometry of the novel phosphinocarbonyl ligand, which is attached to the ruthenium via a Ru–C single bond (2.107 (3) Å). In **8** the corresponding Ru–C bond length is found to be 2.084 (7) Å, indicating no significant π-back-bonding from the metal to the carbamoyl ligand. The $RuC(CH_2)$ single bond in $[(\eta^5\text{-}C_5H_5)(CO)_2Ru]_2CH_2$ (**9**) (2.18 Å), however, exceeds those in **5b** and **8**.[12]



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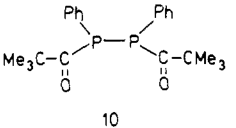
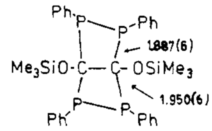
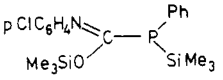


10

Unlike the planar $C(O)NH_2$ arrangement in **8**, the phosphorus in **5b** has a pyramidal configuration. The P–C(CO) distance of 1.952 (3) Å is extremely long compared to a standard P–C single bond (ca. 1.85 Å).[13] This bond elongation cannot be explained by the electronegative character of the heteroatom at carbon as in (trifluoromethyl)phosphines[14] or **10**[15] where the P–C bond lengths are also lengthened from 1.85 to 1.91 Å or to 1.89 Å, respectively. In our opinion the long P–C bond in **5b** also reflects the severe steric strain in the complex. In compound **11** one of the endocyclic P–C bonds is also stretched as a result of steric congestion,[16] and the same is assumed for several other diphosphetanes.[17]

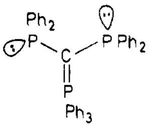


11



12

The carbon atoms of the ketonic CO groups in **5b** and **10** are essentially sp^2-hybridized, and the CO bond distance of 1.219 (4) Å excludes π-conjugation with the lone pair on phosphorus. In **8** the CO distance of the carbamoyl ligand was found to be 1.244 (8) Å.[11] The phosphorus-silicon distance (2.226 (2) Å) is shorter than the corresponding data (2.25–2.30 Å) found in a series of silylphosphines (e.g., 2.278 (1) Å in **12**)[18] and is comparable with the P–Si bond length in $F_3Si\text{-}PH_2$ (2.207 (3) Å)[19] determined by electron diffraction. There is no significant bonding interaction between the silicon and the oxygen atom of the phosphinocarbonyl group as evidenced by a distance of 3.651 Å between these atoms which is about the sum of the van der Waals radii (1.52 and 2.10 Å for O and Si, respectively).[20] The lone pair of the pyramidal phosphorus atom in **5b** is directed between the two terminal carbonyl ligands, thus minimizing an interaction with the π-electron cloud of the ketonic carbonyl group. These observations are consistent with conclusion on the conformation of phosphino-substituted phosphorus ylides such as **13** recently reported by Schmidbaur and coworkers.[21] Temperature-dependent ^{31}P NMR studies revealed a hindered rotation of the PPh_2 groups around the P–C bonds. It was assumed that nonbonding interactions between the sp^2 configured ylidic carbon atom and the lone pairs on the phosphorus atoms could account for a preferred conformation such as **13** at low temperature. This was confirmed by an X-ray diffraction study of crystalline **13**. The molecule has an almost planar $P{=}CP_2$ skeleton, with the lone pairs of electrons of the trivalent phosphorus atoms having their preferred orientation in the $P{=}CP_2$ plane, thus minimizing antibonding interactions.[21]



13

The distortion of the piano stool, reflecting steric crowding in the ligand sphere of the ruthenium atom, is also shown by the nonequivalent angles between the phosphinocarbonyl group and the CO ligands (81.8 (2) and 93.9 (1)°).

Acknowledgment. Generous support of this work by the Deutsche Forschungsgemeinschaft (Bonn), Fonds der Chemischen Industrie, and the Degussa AG, Hanau, Germany, is gratefully acknowledged.

Registry No. **1a**, 59624-91-8; **1b**, 89982-51-4; **1c**, 79908-20-6; **5a**, 98526-72-8; **5b**, 98526-70-6; **5c**, 98526-73-9; **6a**, 97889-65-1; **6b**, 98539-90-3; **6c**, 98526-71-7; $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2$, 70669-56-6; $(\eta^5\text{-}C_5Me_5)Ru(CO)_2Br$, 90420-05-6; $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+BF_4^-$, 86853-54-5.

Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic thermal parameters and structure factors (23 pages). Ordering information is given on any current masthead page.

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