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Complexes of Functional Phosphines. 5.[1] Rhodium(III) and Ruthenium(II) Complexes of Ethyl (Diphenylphosphino)acetate. Synthesis, Dynamic Behavior, and Crystal Structure of *trans*-$\overline{RuCl_2[Ph_2PCH_2C(O}$$)OC_2H_5][Ph_2PCH_2C(O)OC_2H_5]_2$. Reversible CO Coordination on a Ruthenium(II) Complex

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The coordination properties of $Ph_2PCH_2C(O)OC_2H_5$ ($P\frown O$) have been investigated toward Rh(III) and Ru(II) centers. Displacement of a nitrile ligand of $RuCl_3(o\text{-}CH_3C_6H_4CN)_3$ by $P\frown O$ leads to the complex *trans,trans,trans*-$RuCl_2(o\text{-}CH_3C_6H_4CN)_2(P\frown O)_2$ (**1**) in which $P\frown O$ behaves as a monodentate ligand through the phosphorus. Reaction of $RhCl_3(P\frown O)_2$ (**2**) with $AgPF_6$ in acetone converts a monodentate $P\frown O$ into a bidentate $P\frown O$, affording $[RhCl_2(Ph_2PCH_2C(O)OC_2H_5)_2]PF_6$ (**3**). Whereas **2** exhibits stereodynamic behavior on the NMR time scale, **3** does not. Reaction of $P\frown O$ with "ruthenium trichloride" in hot ethanol leads to *trans*-$\overline{RuCl_2[Ph_2PCH_2C(O}$$)OC_2H_5][Ph_2PCH_2C(O)OC_2H_5]_2$ (**4**). The molecular structure of **4** has been determined by X-ray diffraction: triclinic, space group $P\bar{1}$ with $Z = 2$, $a = 11.829$ (4) Å, $b = 12.896$ (2) Å, $c = 16.909$ (7) Å, $\alpha = 91.43$ (2)°, $\beta = 93.74$ (3)°, $\gamma = 112.26$ (2)°, d(calcd) = 1.37 g/cm³. The structure was solved by using 8342 reflections with $I > \sigma(I)$ and refined to conventional $R = 0.043$. The Ru atom has a distorted octahedral environment with trans Cl atoms (Ru–Cl = 2.419 (1) Å) and *mer* P atoms. The two monodentate $P\frown O$ ligands (Ru–P(1) = 2.403 (1), Ru–P(3) = 2.266 (1) Å) are cis to each other, and the chelating $P\frown O$ has P(2) trans to P(1) (Ru–P(2) = 2.363 (1) Å) and O(3) trans to P(3). The long Ru–O(3) distance (2.230 (3) Å), together with the short Ru–P(3) bond, is consistent with the weak trans influence of the ester oxygen donor atom. The hemilabile character of $P\frown O$ in this complex is evidenced by its stereodynamic behavior, resulting from the easy rupture of the Ru–O(3) bond. In the ^{31}P NMR, coalescence of the signals due to P(1) and P(2) occurred at 315 K ($\Delta G^{\ddagger} = 13.3$ kcal/mol). Another coalescence phenomenon was observed at 193 K resulting from conformational changes within the organic backbones of the ligands ($\Delta G^{\ddagger} = 8.5$ kcal/mol). Bubbling CO through a solution of **4** in CH_2Cl_2 under ambient conditions affords *trans,trans,trans*-$RuCl_2(CO)_2(P\frown O)_2$ (**5**), in which the remaining $P\frown O$ ligands are both monodentate through the phosphorus. Chelation of one of these $P\frown O$ ligands occurs by removal of one coordinated CO. This is facilitated by bubbling nitrogen through a solution of **5** in CH_2Cl_2, affording $\overline{RuCl_2(CO)[Ph_2PCH_2C(O}$$)OC_2H_5][Ph_2PCH_2C(O)C_2H_5]$ (**6**). Conversely, **6** will take up CO under ambient conditions and regenerate **5**. The ease with which **6** reversibly binds CO is related to the electronic and structural properties of the $P\frown O$ ligand. All complexes were characterized by elemental analysis and IR, ^1H NMR, and $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

Transition-metal complexes of functional phosphines attract considerable interest because of their structural features, reactivity, and catalytic applications. These phosphines, sometimes called "hybrid"[3,4] or "mixed" ligands,[5] combine a soft phosphine donor and a functional group into a potentially bidentate array. Such ligands have recently been used as bridges in bimetallic complexes[6] and as unsymmetrical chelates[7–9] and have led to the discovery of new complexes of unique reactivity.[10,11] Particularly noteworthy are the examples where tertiary phosphines containing an oxygen donor function (e.g., ether,[12–14] enolate,[11,15] acetate,[1] carboxylic acids[4]) were used. Catalytic application of related complexes includes, for example, the Monsanto L-Dopa synthesis[14] using phosphine anisoles and the Shell ethylene oligomerization process using benzoic or carboxyalkyl phosphines.[16]

We have previously shown that ethyl (diphenylphosphino)acetate, $Ph_2PCH_2C(O)OC_2H_5$, can behave either as a monodentate ligand coordinated through the phosphorus atom or as a chelate, depending upon the nature of the transition metal used and of its environment.[1] Futhermore, an intermediate situation has been characterized in which two such ligands coordinated to Rh(III), one monodentate (through the phosphorus) and the other chelate, exchange their role through easy metal–oxygen bond cleavage.[9] This illustrates the possible hemilabile character of $Ph_2PCH_2C(O)OC_2H_5$. We present here further investigations of the coordination chemistry of this ligand with Rh(III) and Ru(II). In the latter case, a new complex was obtained for which its reversible CO uptake in solution in discussed in the light of the hemilabile behavior of the ligand $Ph_2PCH_2C(O)OEt$($P\frown O$). The X-ray structure determination of *trans*-$\overline{RuCl_2[Ph_2PCH_2C(O}$$)OEt][Ph_2PCH_2C(O)OEt]_2$ is also presented.

Experimental Section

A. Reagents and Physical Measurements. All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were

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distilled under nitrogen and dried prior to use. Nitrogen (Air Liquide purified grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. CO was purchased from Air Liquide.

Elemental analyses of C, H, N, and F were performed by the Service Central de Microanalyses du CNRS.

Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer as KBr pellets (unless otherwise specified) and on a Polytec FIR 30 FT interferometer as polythene disks in the region 420–50 cm^{-1}.

The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 90.00 and/or 250.00 and at 36.43 MHz, respectively, on a FT Bruker WH-90 or Cameca 250 instrument. Proton chemical shifts are positive downfield relative to external Me$_4$Si. Positive phosphorus chemical shifts indicate a downfield position relative to H$_3$PO$_4$.

B. Synthesis. Ph$_2$PCH$_2$C(O)OC$_2$H$_5$ (P$\frown$O) was prepared by the method described previously.[1,9]

***trans,trans,trans*-RuCl$_2$(*o*-CH$_3$C$_6$H$_4$CN)$_2$(Ph$_2$PCH$_2$C(O)OC$_2$H$_5$)$_2$ (1).** To a boiling solution of 0.12 g (0.37 mmol) of RuCl$_3$(*o*-CH$_3$C$_6$H$_4$CN)$_3$[17] in 30 mL of methanol was added a solution of 0.303 g (1.11 mmol) of Ph$_2$PCH$_2$C(O)OC$_2$H$_5$ in methanol (5 mL). After a 1-h reaction time, the solution was cooled and kept at −10 °C. The orange, air-stable crystals of **1**, which precipitated (0.15 g, 52%), were collected, washed with diethyl ether, and dried under vacuum; mp 162–165 °C; IR (KBr) ν(CN) 2227 s, ν(CO) 1719 vs cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.83 (t, CH$_2$C*H*$_3$, ^3J = 7.3 Hz), 2.27 (s, *o*-CH$_3$), 3.65 (q, C*H*$_2$CH$_3$, ^3J = 7.2 Hz), 4.00 (virtual t, ^{2+4}J(PH) = 16.5 Hz); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 26.4. Anal. Calcd for C$_{48}$H$_{48}$Cl$_2$N$_2$O$_4$P$_2$Ru: C, 60.62; H, 5.09; N, 2.94. Found: C, 60.38; H, 5.27; N, 3.17.

[RhCl$_2$(Ph$_2$PCH$_2$C(O)OC$_2$H$_5$)$_2$]PF$_6$ (3). To a stirred solution of 0.155 g (0.21 mmol) of RhCl$_3$(P$\frown$O)$_2$[9] (**2**) in 20 mL of acetone was added a suspension of 0.053 g (0.21 mmol) of AgPF$_6$ in acetone (10 mL). The solution immediately became turbid and after 0.2 h was carefully filtered. Then pentane was added, and after the solution was cooled to −10 °C, orange-red crystals of **3** were produced (0.162 g, 91%). These were recrystallized several times from acetone/pentane and dried: mp 181–183 °C; IR (KBr) ν(CO) 1622 s, ν(PF) 840 s, br, ν(Rh–Cl) 369 vs, 348 m cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 1.53 (t, CH$_2$C*H*$_3$, ^3J = 7.2 Hz), 4.32 (filled-in doublet, PCH$_2$, Δ(external lines) = 13.5 Hz), 4.77 (q, C*H*$_2$CH$_3$, ^3J = 7.2 Hz); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 34.1 (d, ^1J(Rh–P) = 122 Hz), −149.7 (sept, ^1J(PF) = 710 Hz). Anal. Calcd for C$_{32}$H$_{34}$Cl$_2$F$_6$O$_4$P$_3$Rh: C, 44.52; H, 3.97; F, 13.20. Found: C, 43.99; H, 3.90; F, 11.96.

***trans*-RuCl$_2$(Ph$_2$PCH$_2$C(O)OC$_2$H$_5$)(Ph$_2$PCH$_2$C(O)OC$_2$H$_5$)$_2$ (4).** To a boiling solution of 2.18 g (8 mmol) of Ph$_2$PCH$_2$C(O)OC$_2$H$_5$ in 100 mL of ethanol was added 0.51 g (1.91 mmol) of "ruthenium trichloride" (38% Ru) dissolved in 50 mL of ethanol. The solution turned dark red. After a 2-h reflux, the solution was concentrated and hexane was added. Cooling to −10 °C afforded **4** as brick red air-stable crystals (0.940 g, 49.7%), which were recrystallized from ethanol/hexane: mp 115–116 °C; IR ν(CO) 1719 vs and 1641 vs, ν_{as}(RuCl) 316 s cm^{-1}; ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 243 K) ABX spin system δ_A 18.2, δ_B 36.3, δ_X 53.3 (J(AX) = 33 Hz, J(BX) = 32 Hz, J(AB) = 332 Hz); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 213 K) δ 12.75 (s, CH$_3$), 12.99 (s, CH$_3$), 13.33 (s, CH$_3$), 31.35 (d, PCH$_2$, ^1J(PC) = 11 Hz), 37.82 (d, PCH$_2$, ^1J(PC) = 20 Hz), 41.05 (d, PCH$_2$, ^1J(PC) = 27 Hz), 60.21 (s, *C*H$_2$CH$_3$), 60.32 (s, *C*H$_2$CH$_3$), 65.17 (s, *C*H$_2$CH$_3$), 126.64–133.92 (aromatic C), 167.97 (d, C═O), 168.88 (d, C═O), 181.02 (d, C═O). For further NMR details, see text. Anal. Calcd for C$_{48}$H$_{51}$Cl$_2$O$_6$P$_3$Ru: C, 58.30; H, 5.35. Found: C, 58.25; H, 5.24.

***trans,trans,trans*-RuCl$_2$(CO)$_2$(Ph$_2$PCH$_2$C(O)OC$_2$H$_5$)$_2$ (5).** Carbon monoxide was bubbled for 1 min through a solution of 0.500 g (0.51 mmol) of RuCl$_2$(Ph$_2$PCH$_2$C(O)OC$_2$H$_5$)$_3$ (**4**) in 10 mL of CH$_2$Cl$_2$. The yellow solution was then cooled under CO at −10 °C, affording yellow crystals (0.37 g, 93%) of **5**, which were washed with diethyl ether and dried: mp > 130 °C; IR (KBr) ν(C≡O) 2025 s, ν(C═O) 1725 s cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 0.95 (t, CH$_3$, ^3J = 7.2 Hz), 3.85 (q, C*H*$_2$CH$_3$, ^3J = 7.2 Hz), 3.89 (virtual t, PCH$_2$, ^{2+4}J(PH) = 7.6 Hz); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 18.6. Anal. Calcd for C$_{34}$H$_{34}$Cl$_2$O$_6$P$_2$Ru: C, 52.86; H, 4.44. Found: C, 52.85; H, 4.47.

RuCl$_2$(CO)(Ph$_2$PCH$_2$C(O)OC$_2$H$_5$)(Ph$_2$PCH$_2$C(O)OC$_2$H$_5$) (6). A 0.200-g sample (0.26 mmol) of RuCl$_2$(CO)$_2$(Ph$_2$PCH$_2$C(O)OC$_2$H$_5$)$_2$ (**5**) was dissolved in 20 mL of CH$_2$Cl$_2$, and N$_2$ was bubbled for 5 min through the solution. Slow crystallization afforded yellow crystals (0.184 g, 95%) of analytically pure RuCl$_2$(CO)(Ph$_2$PCH$_2$C(O)OC$_2$H$_5$)$_2$ (**6**): IR (KBr) ν(C≡O) 1952 br, s, ν(C═O) 1727 s and 1633 s cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 0.92 (t, CH$_3$, ^3J = 7.2 Hz), 1.11 (t, CH$_3$, $^3J \simeq$ 7 Hz); ^{31}P NMR (CD$_2$Cl$_2$) AB pattern δ_A 31.2, δ_B 37.8 (^2J(P–P) = 375 Hz). Anal. Calcd for C$_{33}$H$_{34}$Cl$_2$O$_5$P$_2$Ru: C, 53.23; H, 4.60. Found: C, 53.16; H, 4.55.

Table I. Summary of Crystal and Intensity Collection Data of **4**

compd	*trans*-RuCl$_2$[Ph$_2$PCH$_2$C(O)OC$_2$H$_5$]-[Ph$_2$PCH$_2$C(O)OC$_2$H$_5$]$_2$
formula	C$_{48}$H$_{51}$Cl$_2$O$_6$P$_3$Ru
fw	988
cryst system	triclinic
a, Å	11.829 (4)
b, Å	12.896 (2)
c, Å	16.909 (7)
α, deg	91.43 (2)
β, deg	93.74 (3)
γ, deg	112.26 (2)
V, Å^3	2378.6 (5)
Z	2
d(calcd), g cm^{-3}	1.37
cryst dimens, mm	0.1 × 0.1 × 0.08
space group	$P\bar{1}$
temp, °C	25
radiation	Mo Kα from monochromator λ(Mo Kα_1) = 0.709 26 Å
linear abs coeff, cm^{-1}	57.5
scan range, deg	0.7 + 0.35 tan θ
2θ limits, deg	6–60
scan θ/scan ω	$^1/_2$
data collected	10 890
unique data used	8342 ($I > \sigma(I)$)
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.043

C. Collection of the X-ray Data and Structure Determination. Well-formed crystals were grown by slow diffusion of hexane into an ethanol solution of **4**. Cell constants and other pertinent data are presented in Table I. Intensity data were collected on a Nonius CAD 4 diffractometer. No intensity decay was observed during the data collection period, as shown by the systematic measure of 3 standard reflections after every 50 reflections. The scan rate, based on a prescan (0.833° s^{-1}), was computed such that 10^4 counts were obtained in a maximum allowed time of 120 s. The net intensities have been corrected for Lorentz and polarization factors. Absorption corrections were omitted in view of the low linear absorption coefficient. The structure was solved by Patterson and Fourier methods. Refinements by full-matrix least-squares methods have been done with all non-hydrogen atoms isotropic. Then, in order to avoid excessive computer time, the positional parameters and anisotropic vibrational parameters were refined blockwise, successively for the atoms Ru, Cl(1), Cl(2), P(1), P(2), and P(3) and then for each of the groups RuPPh$_2$CH$_2$COOC$_2$H$_5$. A final least-squares cycle refined the positional parameters without the anisotropic vibrational parameters. Atomic coordinates with standard deviations corresponding to the final least-squares refinement cycle are given in Table II. This refinement has proceeded to the unweighted *R* factor value 0.0428, using the SHELX[18] method. Thermal parameters for non-hydrogen atoms (Table V) and a listing of the observed structure factor amplitudes of the reflections used in the refinement (Table VI) are available as supplementary material.[19]

Results and Discussion

Addition of Ph$_2$PCH$_2$C(O)OC$_2$H$_5$ (P$\frown$O) to RuCl$_3$(*o*-CH$_3$C$_6$H$_4$CN)$_3$ in hot methanol solution produces orange *trans,trans,trans*-RuCl$_2$(*o*-CH$_3$C$_6$H$_4$CN)$_2$(P$\frown$O)$_2$ (**1**) in good yield. Spectroscopic data, in particular the presence of a virtual triplet assignable to the PCH$_2$ protons (see Experimental

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(18) SHELX crystallographic calculation program, G. M. Sheldrick, University of Göttingen, Göttingen, West Germany.

(19) See paragraph at the end of the paper regarding supplementary material.

Table II. Atomic Fractional Coordinates for **4**[a]

atom[b]	10^4x	10^4y	10^4z
Ru	4574.0 (3)	1640.5 (2)	2530.6 (2)
Cl(1)	3833 (1)	2143 (1)	3721 (1)
Cl(2)	5684 (1)	1108 (1)	1553 (1)
P(1)	3052 (1)	−234 (1)	2518 (1)
P(2)	6357 (1)	3303 (1)	2676 (1)
P(3)	3420 (1)	2321 (1)	1743 (1)
O(1)	666 (4)	−1488 (4)	4014 (2)
O(2)	580 (5)	−2390 (3)	2883 (3)
O(3)	5784 (2)	1100 (2)	3345 (2)
O(4)	7677 (3)	1190 (3)	3674 (2)
O(5)	2442 (4)	4544 (3)	2541 (2)
O(6)	2395 (6)	4405 (5)	1250 (3)
C(1)	1642 (4)	−362 (4)	3004 (3)
C(2)	906 (4)	−1527 (4)	3265 (3)
C(3)	−142 (7)	−2553 (6)	4317 (5)
C(4)	543 (12)	−3045 (9)	4742 (8)
C(5)	3589 (4)	−1127 (3)	3142 (3)
C(6)	3780 (5)	−2071 (4)	2855 (3)
C(7)	4206 (6)	−2691 (4)	3380 (4)
C(8)	4443 (5)	−2379 (4)	4188 (3)
C(9)	4229 (4)	−1454 (4)	4477 (3)
C(10)	3816 (4)	−827 (4)	3960 (3)
C(11)	2493 (4)	−1039 (3)	1572 (3)
C(12)	3349 (5)	−1252 (4)	1119 (3)
C(13)	2994 (6)	−1778 (4)	360 (3)
C(14)	1789 (6)	−2092 (5)	44 (3)
C(15)	927 (5)	−1899 (4)	487 (3)
C(16)	1273 (4)	−1364 (4)	1262 (3)
C(17)	7518 (3)	2728 (3)	3022 (3)
C(18)	6893 (4)	1600 (3)	3359 (2)
C(19)	7147 (5)	43 (4)	3963 (4)
C(20)	8135 (6)	−349 (5)	4151 (5)
C(21)	6668 (5)	4164 (4)	4245 (3)
C(22)	6530 (4)	4383 (3)	3451 (3)
C(23)	6448 (4)	5401 (4)	3255 (4)
C(24)	6508 (5)	6195 (5)	3856 (4)
C(25)	6634 (5)	5964 (5)	4650 (4)
C(26)	6715 (5)	4956 (5)	4846 (4)
C(27)	7128 (4)	4138 (3)	1869 (3)
C(28)	6659 (4)	3820 (3)	1085 (3)
C(29)	7283 (5)	4416 (4)	464 (3)
C(30)	8400 (5)	5326 (4)	627 (4)
C(31)	8877 (5)	5650 (5)	1419 (4)
C(32)	8239 (4)	5062 (4)	2040 (3)
C(33)	3826 (4)	3831 (3)	2038 (3)
C(34)	2839 (5)	4307 (4)	1869 (3)
C(35)	1386 (6)	4909 (6)	2436 (5)
C(36)	1012 (7)	4947 (9)	3277 (6)
C(37)	1748 (3)	1751 (3)	1806 (3)
C(38)	1291 (4)	1966 (4)	2508 (3)
C(39)	25 (4)	1551 (5)	2573 (3)
C(40)	−781 (4)	910 (5)	1949 (4)
C(41)	−332 (4)	680 (5)	1252 (3)
C(42)	930 (4)	1107 (4)	1175 (3)
C(43)	3531 (4)	2289 (4)	662 (3)
C(44)	3618 (5)	3194 (5)	204 (3)
C(45)	3698 (7)	3104 (6)	−616 (4)
C(46)	3692 (6)	2114 (6)	−974 (3)
C(47)	3594 (5)	1203 (5)	−518 (3)
C(48)	3524 (4)	1291 (4)	302 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant figures. [b] Atoms are labeled to agree with Figure 2.

Section) as well as the presence of a single CN absorption band (IR (KBr)) at 2227 cm^{-1}, are consistent with the proposed trans,trans,trans structure. The observed ν(CO) frequency at 1719 cm^{-1} is typical for a noncoordinating ester function. Prolonged heating of a solution of **1** does not lead to dissociation of the nitrile ligand(s) with subsequent chelation of the phosphine(s). However, chelating behavior has already been observed for P͡O in the isoelectronic Rh(III) complex $RhCl_3(PPh_2CH_2C(O)OC_2H_5)(Ph_2PCH_2C(O)OC_2H_5)$ (**2**).[9] In this case, the coordinated ester dissociates easily in solution, exchanging its role with the second ester function. This complex reacts with an excess of $AgPF_6$, according to eq 1.

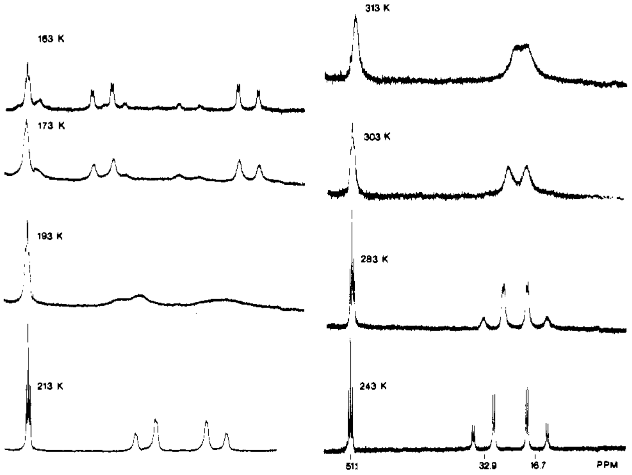
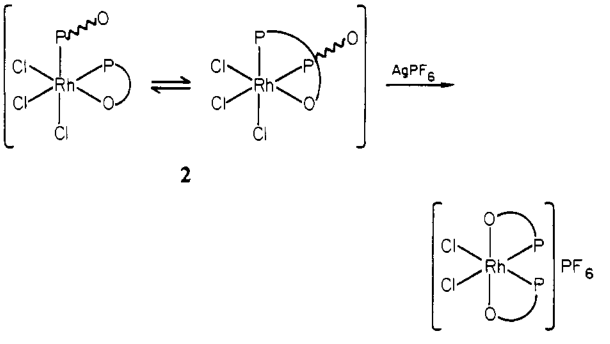


Figure 1. Variable temperature $^{31}P\{^1H\}$ NMR spectrum of $RuCl_2[Ph_2PCH_2C(O)OC_2H_5][Ph_2PCH_2C(O)OC_2H_5]_2$ (**4**) from 313 to 163 K.



2

(1)

3

The orange complex **3** is soluble in dichloromethane or acetone. Its infrared spectrum shows a single ν(C=O) band at 1622 cm^{-1}. This, coupled with the absence of the band at 1719 cm^{-1}, suggests that the two ester functions are coordinated in equivalent sites. The two Rh–Cl stretching vibrations are consistent with mutually cis chlorines. In the $^{31}P\{^1H\}$ NMR spectrum, the presence of a doublet (δ 34.1, ^1J(RhP) = 122 Hz) is consistent with two equivalent phosphorus atoms. The PCH_2 protons appear as a filled-in doublet, a pattern frequently observed when two PPh_2CH_3 or PPh_2CH_2[20a] units are in cis position.[20b] Although the structure is not unambiguously established, a structure of type **3**, in which the two oxygens occupy mutually trans positions, is consistent with all the data.

We were of course interested in taking advantage of the hemilabile character of P͡O for coordinating small molecules like CO. The failure to observe this with **2** and **3** probably originates from the low affinity of the Rh(III) center toward CO. With the aim of obtaining new complexes that combine the stabilizing effect of the potential chelation of P͡O and the lability of at least one metal–ester bond with the affinity of

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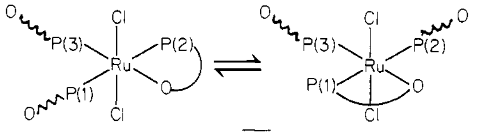
(20) (a) Redfield, D. A.; Nelson, J. H. *Inorg. Chem.* **1973**, *12*, 15. (b) Verstuyft, A. W.; Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Ibid.* **1977**, *16*, 2776.

(21) The ^{13}C NMR spectrum at 213 K of **4** shows three doublets in the carbonyl region at respectively 167.97, 168.88, and 181.02 ppm. When NMR data[1,22] of coordinated and uncoordinated esters are used, the doublet at 181 ppm may reasonably be assigned to a coordinated ester. Although the coordination of the OEt group of –COOEt seems very unlikely, this possibility cannot totally be ruled out.

(22) Brown, J. M.; Chaloner, P. A. *J. Chem. Soc., Chem. Commun.* **1980**, 344.

Scheme I. Dynamic Behavior of 4 Exchanging P(1) and P(2)



the metal center for CO, we have prepared a Ru(II) complex by reacting excess P⌒O with commercial ruthenium trichloride (eq 2).

$$\text{“RuCl}_3\text{”} + 4\mathrm{Ph_2PCH_2C(O)OC_2H_5} \xrightarrow[\Delta,2\mathrm{h}]{\mathrm{EtOH}} \underset{\mathbf{4}}{\mathrm{RuCl_2(Ph_2PCH_2C(O)OC_2H_5)(Ph_2PCH_2COOC_2H_5)_2}} \quad (2)$$

The IR spectrum of **4** shows the presence of both coordinated and uncoordinated C=O (1712 vs, 1641 vs cm^{-1}).[21] The ^{31}P NMR spectrum (CD_2Cl_2 + 10% toluene, 243 K) displays a characteristic ABX pattern (see Figure 1). The attribution of the resonances at 16.7 and 32.9 ppm to the couple [P(1), P(2)] results from the ^2J[P(1), P(2)] value (333 Hz), in keeping with two phosphorus atoms in trans position. This structure has also been found in the solid state as shown by a crystal structure determination (see below). When the temperature was raised, the signals of P(1) and P(2) first broadened and then coalesced at ca. 313 K, their coupling with P(3) remaining constant. The observed phenomenon was temperature reversible, and the calculated ΔG^* value[23] is 13.3 kcal/mol. These observations[24] may be explained by a rapid exchange in the chelating behavior of the two phosphines in trans position, according to Scheme I.

By lowering the temperature, a new coalescence phenomenon was observed at 193 K. All signals of the previously described ABX system separate when the temperature reached ca. 173 K. The ratio of the interconverting species is 1:4, and the calculated ΔG^* values[23] are respectively 8.8 kcal/mol for $P(3)' \rightleftharpoons P(3)''$, 8.7 kcal/mol for $P(2)' \rightleftharpoons P(2)''$ and 8.2 kcal/mol for $P(1)' \rightleftharpoons P(1)''$, where the primes and double primes refer to the two interconverting species and the numbering of the phosphorus atoms corresponds to that in the higher temperature species.

For the two "new" species, the coupling constants between the different phosphorus atoms remain very similar to those found in the species described above, indicating that their structures are analogous. We therefore conclude that this low-energy exchange process must be assigned to conformational changes within the organic backbones of the ligands.

When a CH_2Cl_2 solution of complex **4** was treated with CO (1 atm), formation of **5** instantaneously occurred.

In the ^{1}H NMR (CD_2Cl_2) spectrum of **5**, the presence of a virtual triplet at 3.82 ppm (PCH_2) indicates a trans P–Ru–P array. The trans OC–Ru–CO arrangement was deduced from the IR spectrum (KBr), showing only one strong ν(C≡O) absorption band (2025 cm^{-1}). This reaction, when followed by ^{31}P NMR, revealed (eq 3) that, besides **5**, small amounts

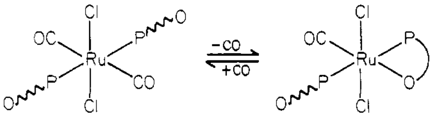
$$\underset{\mathbf{4}}{\mathrm{RuCl_2(Ph_2PCH_2C(O)OC_2H_5)_3}} + \mathrm{CO} \xrightarrow{\mathrm{CH_2Cl_2}} \underset{\mathbf{5}}{\mathrm{RuCl_2(CO)_2(Ph_2PCH_2C(O)OC_2H_5)_2}} + \mathbf{6} + \mathrm{Ph_2PCH_2C(O)OC_2H_5} \quad (3)$$

of complex **6** were formed. The structure of **6** could unambiguously be established by spectroscopic data (see Experimental Section).

Table III. Selected Interatomic Distances (Å) and Angles (deg) in 4

Ru–Cl(1)	2.419 (1)	P(2)–C(17)	1.863 (4)
Ru–Cl(2)	2.419 (1)	C(17)–C(18)	1.504 (5)
Ru–P(1)	2.403 (1)	C(18)–O(4)	1.320 (5)
Ru–P(2)	2.363 (1)	C(18)–O(3)	1.222 (4)
Ru–P(3)	2.266 (1)	O(4)–C(19)	1.480 (5)
Ru–O(3)	2.230 (3)	C(19)–C(20)	1.461 (7)
P(1)–C(1)	1.862 (4)	P(3)–C(33)	1.868 (4)
C(1)–C(2)	1.517 (6)	C(33)–C(34)	1.528 (6)
C(2)–O(1)	1.320 (6)	C(34)–O(5)	1.331 (6)
C(2)–O(2)	1.188 (6)	C(34)–O(6)	1.170 (6)
O(1)–C(3)	1.470 (7)	O(5)–C(35)	1.495 (6)
C(3)–C(4)	1.383 (13)	C(35)–C(36)	1.524 (11)
C–C (phenyls)	av 1.400 (7)		
Cl(1)–Ru–Cl(2)	166.67 (5)	C(2)–O(1)–C(3)	116.0 (5)
P(1)–Ru–P(3)	167.33 (5)	O(1)–C(3)–C(4)	110.3 (7)
P(3)–Ru–O(3)	175.74 (7)	O(1)–C(2)–O(2)	121.7 (5)
P(1)–Ru–Cl(1)	90.35 (5)	Ru–P(2)–C(17)	100.5 (1)
P(1)–Ru–Cl(2)	92.24 (5)	P(2)–C(17)–C(18)	109.9 (9)
P(2)–Ru–Cl(1)	91.45 (5)	C(17)–C(18)–O(4)	112.7 (3)
P(2)–Ru–Cl(2)	83.24 (5)	C(17)–C(18)–O(3)	124.6 (4)
P(3)–Ru–Cl(1)	92.18 (5)	C(18)–O(4)–C(19)	116.5 (3)
P(3)–Ru–Cl(2)	100.57 (5)	O(4)–C(19)–C(20)	108.8 (4)
P(1)–Ru–P(3)	95.53 (5)	O(4)–C(18)–O(3)	122.7 (4)
P(2)–Ru–P(3)	96.93 (5)	C(18)–O(3)–Ru	119.0 (3)
Cl(1)–Ru–O(3)	86.0 (1)	Ru–P(3)–C(33)	108.9 (1)
Cl(2)–Ru–O(3)	81.1 (1)	P(3)–C(33)–C(34)	117.0 (3)
P(1)–Ru–O(3)	88.3 (1)	C(33)–C(34)–O(5)	110.8 (4)
P(2)–Ru–O(3)	79.3 (1)	C(33)–C(34)–O(6)	127.8 (5)
Ru–P(1)–C(1)	114.9 (1)	C(34)–O(5)–C(35)	114.9 (5)
P(1)–C(1)–C(2)	114.8 (3)	O(5)–C(35)–C(36)	103.3 (6)
C(1)–C(2)–O(1)	110.8 (4)	O(5)–C(34)–O(6)	121.3 (5)
C(1)–C(2)–O(2)	127.5 (5)		

They indicate the presence of one monodentate ligand and one chelate P⌒O ligand with a trans P–Ru–P arrangement. This latter complex could be obtained in good yield by dissolving **5** in CH_2Cl_2. Loss of one CO occurred after a few hours and was accompanied by chelation of one P⌒O ligand (eq 4).



(4)

5 **6**

Removal of one coordinated CO is facilited by bubbling nitrogen through a solution of **5** in CH_2Cl_2. Conversely, bubbling CO through a solution of **6** instantaneously regenerates **5** via opening of the chelating ligand and CO coordination. This smooth reversible CO uptake under ambient conditions again illustrates the potentiality of hemilabile ligands such as P⌒O when coordinated to appropriate transition metals in some of their molecular complexes. This is of particular significance for the coordination, the activation, and the transfer of small molecules. A very similar reversible CO substitution of an oxygen donor ligand also been observed[25] on ruthenium(II) with *o*-(diphenylphosphino)anisole.

Description of the Structure of *trans*-RuCl$_2$[Ph$_2$PCH$_2$C(O)OC$_2$H$_5$][Ph$_2$PCH$_2$C(O)OC$_2$H$_5$]$_2$ (4). The molecular structure of **4** is shown in Figure 2. Crystal data are given in Table I, interatomic distances and angles in Table III, and least-squares planes in Table IV.

The crystal structure consists of discrete monomeric molecular units separated by normal van der Waals contacts. This

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(23) Calculated with the usual approximation: $\Delta G^* = 4.57T_c(9.97 + \log(T_c/\delta\nu))$.

(24) The variable temperature spectra are essentially the same in CCl_2D–CCl_2D.

(25) Rauchfuss, T. B.; Patino, F. T.; Roundhill, D. M. *Inorg. Chem.* **1975**, *14*, 652.

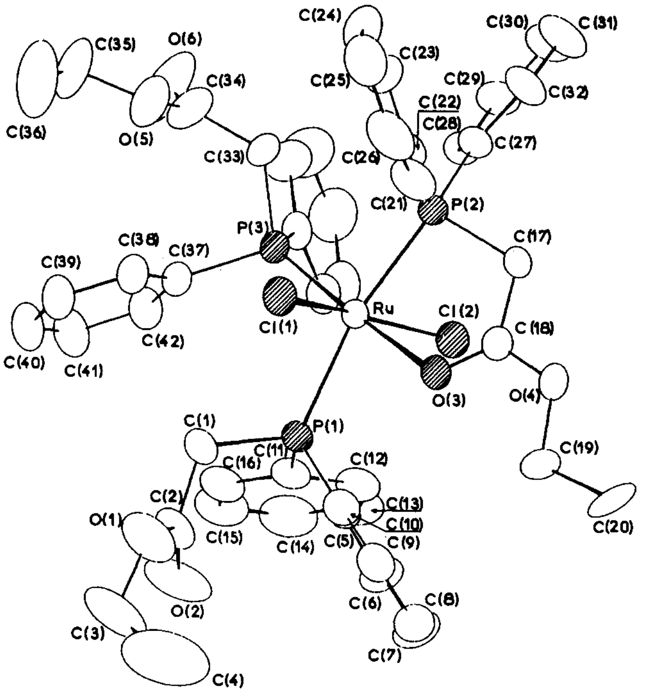

Figure 2. Molecular structure of $\overline{\mathrm{RuCl_2[Ph_2PCH_2C(O)}}\mathrm{OC_2H_5]}$-$\mathrm{[Ph_2PCH_2C(O)OC_2H_5]_2}$ (**4**).

Table IV

Selected Least-Squares Planes for **4**

plane no.	atoms	dist from plane, Å	plane no.	atoms	dist from plane, Å
1	Cl(1)	0.006 (2)	3	Cl(1)	−0.002 (2)
	Cl(2)	0.006 (2)		Cl(2)	−0.002 (2)
	P(1)	−0.006 (2)		P(3)	0.001 (2)
	P(2)	−0.006 (2)		O(3)	0.002 (3)
	Ru[a]	−0.260 (1)		Ru[a]	0.074 (1)
2	P(1)	−0.046 (2)	4	P(2)	−0.01 (1)
	P(2)	−0.042 (2)		C(17)	−0.03 (1)
	P(3)	0.032 (2)		C(18)	0.01 (1)
	O(3)	0.056 (3)		O(3)	−0.05 (1)
	Ru[a]	0.006 (1)		O(4)	0.11 (1)
				C(19)	0.05 (1)
				C(20)	−0.08 (1)

Dihedral Angles between the Planes

plane	angle, deg	plane	angle, deg
1-2	86.5	2-3	87.6
1-3	92.4	2-4	156.0

Equations of the Planes of the Form $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	5.5712	−7.1900	7.6421	61.9296
2	−5.0240	5.0739	9.5836	17.1830
3	8.7325	8.4166	0.7545	44.4956
4	−0.0521	1.0870	2.3974	11.906

[a] This atom was not used in defining the plane.

Ru(II) complex has distorted octahedral geometry with trans chloride ligands, two cis monodentate phosphorus bonded $\widehat{\mathrm{PO}}$ ligands, and one $\widehat{\mathrm{PO}}$ chelate. There are significant angular distortions from the ideal interligand angles (90°) due to the chelate $\widehat{\mathrm{PO}}$ bite angle of 79.3 (1)° and to symmetrical bending of Cl(1) and Cl(2) toward O(3) and away from P(3) (Cl(1)–Ru–Cl(2) = 166.7°), probably in order to minimize nonbonded interactions with the phenyl groups.

The chelate $\widehat{\mathrm{PO}}$ bite angle in this complex is very similar to that found for the ligand *o*-(diphenylphosphino)anisole in the related $\mathrm{RuCl_2[Ph_2P(\textit{o}\text{-}C_6H_4OCH_3)]_2}$ complex, **7** (78.81 and 79.47° for the two chelates).[13]

The different nature of the donor atoms of the $\widehat{\mathrm{PO}}$ bidentate chelate in **4** is reflected in the significantly different Ru–P(1) and Ru–P(3) distances, 2.403 (1) and 2.266 (1) Å, respectively. The latter is considerably shorter than Ru–P(2) or than the Ru–P distance usually found in six-coordinate Ru(II) complexes with mutually trans phosphines[26] (around 2.4 Å). This can be related to the low trans influence of the ester oxygen O(3), which does not compete significantly with P(3) for bonding overlap with Ru.

A similar situation has been noted for ether oxygen atoms in **7**. Also comparable are the Ru–O distances in **4** (2.230 (3) Å) and in **7** (average 2.278 Å), which are much longer than the sum of the covalent radii (1.99 Å)[27] and suggest a rather weakly coordinated oxygen atom in **4**. This can be related to the stereodynamic behavior of this complex (see above), which shows the easy rupture of the Ru–O(3) bond. An even longer Ru–O bond length of 2.575 (5) Å has been observed in $\mathrm{[RuCl(CH_3)(cod)(P(\textit{o}\text{-}CH_3OC_6H_4)_3)]}$.[28]

The Ru–Cl(1) and Ru–Cl(2) distances of 2.419 (1) Å are in the range found for trans Cl–Ru–Cl arrangements in Ru(II) phosphine complexes.[26]

The distances and angles within the organic ligands are normal. As expected, the >C=O distance for the coordinated ester function is longer (1.222 (4) Å) than for the uncoordinated ones (1.170 (6) and 1.188 (6) Å for C(34)–O(6) and C(2)–O(2), respectively).

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Registry No. **1**, 85709-91-7; **2**, 68778-71-2; **3**, 85709-93-9; **4**, 85709-94-0; **5**, 85709-95-1; **6**, 85709-96-2; $\mathrm{RuCl_3(\textit{o}\text{-}CH_3C_6H_4CN)_3}$, 71904-00-2.

Supplementary Material Available: Thermal parameters (Table V) and observed and calculated structure factors (Table VI) for **4** (55 pages). Ordering information is given on any current masthead page.

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(26) Wilkes, L. M.; Nelson, J. H.; Mitchener, J. P.; Babich, M. W.; Riley, W. C.; Helland, B. J.; Jacobson, R. A.; Cheng, M. Y.; Mc Cusker, L. B.; Seff, K. *Inorg. Chem.* **1982**, *21*, 1376 and references therein.

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