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SYNTHESIS AND STRUCTURE OF $Ru(CO)_4[P(OCH_3)_3]$. THE CONFORMATION OF THE TRIMETHYL PHOSPHITE LIGAND IN COMPLEXES

ROGER E. COBBLEDICK, FREDERICK W.B. EINSTEIN *, ROLAND K. POMEROY *
and EDWARD R. SPETCH

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, V5A 1S6 (Canada)

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Summary

Two methods of preparation of $Ru(CO)_4[P(OCH_3)_3]$ from $Ru_3(CO)_{12}$ and $P(OCH_3)_3$ are described. The crystal structure of the compound has been determined from three-dimensional X-ray data collected by counter methods. The space group is $P2_1/c$ with cell dimensions a 13.225(3), b 7.704(3), c 13.278(4) Å and β 109.82(2)°. Intensity data for 1879 observed reflections were refined by conventional methods to $R = 0.044$. The structure shows that the phosphite ligand does not have three fold symmetry. From a comparison of the infrared spectrum in the carbonyl region of $Ru(CO)_4[P(OCH_3)_3]$ with that of the corresponding $P(OCH_2)_3CC_2H_5$ derivative it is concluded that the asymmetry of the ligand is maintained on the infrared time scale. The ^{13}C and ^1H NMR spectra however indicate the methyl groups are all equivalent on the NMR time scale, even at $-120°C$. The NMR study also indicated there is rapid exchange of the axial and equatorial carbonyl groups in solution.

Introduction

A large number of monomeric iron carbonyl derivatives are known some of which are important as intermediates in organic synthesis [1,2] or catalytic cycles [3]. In contrast the number of monomeric ruthenium carbonyl compounds is much smaller. This is due in part to the fact that $Ru(CO)_5$ readily trimerizes to $Ru_3(CO)_{12}$ in the presence of light [4]. Triruthenium dodecacarbonyl [5] is the usual starting material for ruthenium carbonyl complexes and consequently polynuclear derivatives are often obtained. For example phosphines (PR_3) react with $Ru_3(CO)_{12}$ to give compounds having the formula $Ru_3(CO)_9(PR_3)_3$ [6].

It is often found that second row transition metal complexes are more reactive than the corresponding first and third row analogues. For this reason we have been investigating routes to the five coordinate molecules of the type $Ru(CO)_4L$. Herein we describe the preparation and structure of $Ru(CO)_4[P(OCH_3)_3]$ which reveals the phosphite ligand to have an interesting asymmetry.

Experimental

Unless otherwise stated reactions were carried out under nitrogen. Solvents were scrupulously dried and stored under nitrogen before use. Trimethyl phosphite was distilled from sodium and stored under nitrogen. $Ru_3(CO)_{12}$ was prepared by a literature method [5]. Other compounds were commercially available and used without further purification. High pressure reactions were carried out in a 200 ml general purpose bomb obtained from Parr Instrument Company. Infrared spectra were recorded on a Perkin Elmer 237 instrument fitted with an external recorder. The spectra were calibrated with carbon monoxide. Proton and ^{13}C NMR spectra were recorded on a Varian XL 100 spectrometer. Mass spectra were obtained using a Hewlett-Packard 5985 instrument. Microanalyses were carried out by Mr. M. Yang of this department.

Caution: In view of the highly toxic properties of $Fe(CO)_5$ care should be taken when manipulating $Ru(CO)_5$.

Preparation of $Ru(CO)_4[P(OCH_3)_3]$

To $Ru_3(CO)_{12}$ (0.32 g, 0.5 mmol) in hexane (30 ml) was added $P(OCH_3)_3$ (0.19 g, 1.5 mmol) using a 1 ml syringe. The solution was then pressurized with carbon monoxide (80 atm) and heated at 125°C for 12 h. The autoclave was cooled to room temperature and the gases vented. The pale yellow solution was transferred to a Schlenk tube. An infrared spectrum at this stage indicated that the product consisted mainly of $Ru(CO)_4[P(OCH_3)_3]$ but also traces of $Ru(CO)_5$ and $Ru(CO)_3[P(OCH_3)_3]_2$. Hexane, $Ru(CO)_5$ and any unreacted $P(OCH_3)_3$ were removed on the vacuum line at 0°C. The resulting solid was then sublimed at room temperature and 0.02 mm onto a probe cooled to —78°C. (The sublimation apparatus was protected from the light.) The product $Ru(CO)_4[P(OCH_3)_3]$ (0.44 g, 87%) was obtained as a white solid. The compound may be handled for short periods in air, it does however turn yellow on prolonged exposure, especially to light. It melts at 41—42°C (sealed capillary). Found C = 25.15, H = 2.72, MW = 338 (most abundant peak in mass spectrum); $C_7H_9O_7PRu$ calcd. C = 24.93, H = 2.69, MW = 337.2; $\nu(CO)$ = 2072s, 2002m, 1971s, 1957s cm^{-1} (hexane solution). NMR: $^1H = \delta$ 3.62 ppm, $J(P—H)$ 12.8 Hz ($CDCl_3$ soln); ^{13}C = 203.8 (doublet, $J(P—C)$ = 8 Hz) (CO), 53.8 (OCH_3) * ppm (CCl_2FH soln., TMS internal standard); ^{31}P = 158.8 ppm (downfield from H_3PO_4, external standard). ^1H, ^{13}C and ^{31}P NMR spectra of $Ru(CO)_4[P(OCH_3)_3]$ in CCl_2FH were unchanged at —120°C. Lowering the temperature to —135°C caused broadening of the peaks but this could be attributed to viscosity effects.

The following compounds were prepared in the same manner.

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* Phosphorus coupling not resolved; in d_6-acetone (at —95°C) $J(P—C)$ was observed to be 4 Hz.

$Ru(CO)_4[P(OC_2H_5)_3]$: found C = 32.29, H = 4.44, MW 380; $C_{10}H_{15}O_7PRu$ calcd. C = 31.64, H = 3.99, MW = 379.3; $\nu(CO)$ = 2069s, 2000m, 1967s, 1953s cm^{-1}. The compound is a pale yellow oil at room temperature. $Ru(CO)_4(PPh_3)$: MW found = 476, calcd. 475.4; $\nu(CO)$ = 2061s, 1988m, 1955s, lit [7] = 2060, 1986, 1953 (heptane soln.). $Ru(CO)_4[PPh_2(CH_3)]$: $\nu(CO)$ = 2060s, 1986m, 1948s cm^{-1}. (The last absorption was somewhat broader than the corresponding band of $Ru(CO)_4PPh_3$.)

The method was not suitable for the $P(OCH_2)_3CC_2H_5$, $P(OPh)_3$ or $P(o\text{-tolyl})_3$ derivatives. ($Ru(CO)_5/Ru_3(CO)_{12}$ mixtures were obtained in the last two cases.)

It was also noted that the reaction of $Ru_3(CO)_{12}$ and excess $P(OCH_3)_3$ in hexane solution at room temperature produced (after 24 h) a mixture of $Ru(CO)_4[P(OCH_3)_3]$ and $Ru(CO)_3[P(OCH_3)_3]_2$ ($\nu(CO)$ = 1933vs, 1922vs cm^{-1}) in a ratio of approximately 2 : 1. A third product was present in trace amounts ($\nu(CO)$ = 2029 cm^{-1}).

$Ru(CO)_4[P(OCH_3)_3]$ may be separated from the bis substituted derivative by careful sublimation at room temperature. The latter compound does however sublime at 40°C (0.02 mm).

$Ru(CO)_4[P(OCH_3)_3]$ does not undergo further substitution with $P(OCH_3)_3$ at room temperature.

Preparation of $Ru(CO)_4[P(OCH_2)_3CC_2H_5]$

An autoclave containing $Ru_3(CO)_{12}$ (0.32 g, 0.5 mmol) in hexane (30 ml) was pressurized with carbon monoxide (100 atm) and heated to 130°C for 16 h. The autoclave was then cooled to room temperature and the gases slowly vented. An infrared spectrum at this stage revealed that the product was mainly $Ru(CO)_5$ ($\nu(CO)$ = 2035s, 2000vs, lit [2] 2035s, 1999vs cm^{-1}) with some unreacted $Ru_3(CO)_{12}$. The pale yellow solution was transferred, with the minimum exposure to light, to a Schlenk tube which was then cooled to —78°C for 0.5 h during which time most of the $Ru_3(CO)_{12}$ precipitated from the solution. The almost colorless solution was transferred to a second Schlenk tube containing $P(OCH_2)_3CC_2H_5$ (0.72 g, 4.5 mmol) and stirred for 8 h at room temperature during which time a yellow precipitate formed. The supernatant liquid was removed from the precipitate which was extracted with two 10 ml portions of hot hexane (a sticky yellow solid remained after the extraction). The hexane extracts were combined and cooled to —15°C to yield $Ru(CO)_4[P(OCH_2)_3CC_2H_5]$ (0.10 g, 18%) as almost colorless needles (mp 114—115°C); found C = 32.39, H = 3.38, MW = 376; calcd. C = 32.01, H = 2.95, MW = 375.2. The compound showed no apparent decomposition in air after 24 h, however prolonged exposure caused yellowing of the crystals. The infrared spectrum (2200—1800 cm^{-1} region, hexane solution) showed a minor peak at 2012 cm^{-1} besides the three principal carbonyl stretches (2075s, 2006m, 1977vs cm^{-1}). This peak remained unchanged in intensity on subliming the product at 50°C (0.02 mm) onto a probe cooled to —78°C.

$Ru(CO)_4[P(OCH_3)_3]$ may also be prepared from $Ru(CO)_5$ and $P(OCH_3)_3$ (in good yield).

Crystallographic analysis of $Ru(CO)_4[P(OCH_3)_3]$

Data collection. Colorless crystals suitable for structure analysis were obtained by sublimation under vacuum (closed atmosphere) at room temperature onto a water cooled probe. The crystals were sealed in a glass capillary. Preliminary Weissenberg and precession photographs taken with Cu-K_α radiation showed the crystals to be monoclinic. Systematically absent reflections $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ uniquely indicated the space group $P2_1/c$ (C^5_{2h}). A crystal of approximate dimensions 0.25 × 0.30 × 0.25 mm was chosen for the data collection. The crystal was mounted on a Picker FACS I automated four-circle diffractometer with the b axis slightly offset from the ϕ axis. Cell dimensions were obtained from a least-squares refinement of the setting angles of 12 reflections ($2\theta > 30°$) centered on the diffractometer using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.70926$ Å). The unit cell dimensions were a 13.225(3), b 7.704(3), c 13.278(4) Å, β 109.82(2)° and V 1272 Å^3. The calculated density for $Z = 4$ is 1.760 g cm^{-3}, observed density >1.63 g cm^{-3} (aqueous KI). Integrated diffraction intensities from one quadrant were collected at 23°C using graphite monochromatized Mo-K_α radiation. The θ—2θ scan technique was employed with a scan speed of 2° min^{-1}. A base scan width of 1.5° with an extension to allow for dispersion was used. Backgrounds were counted for 10 sec at each side of the scan for reflections with $2\theta \leqslant 25°$ and for 20 sec for the remaining reflections. Two standard reflections were monitored every 60 reflections and showed no significant variation with time. Intensity data for 2254 unique reflections out to $2\theta = 50°$ were collected but only those 1879 reflections with $I > 2.3\sigma(I)$, where $\sigma(I)$ is the standard deviation estimated from counting statistics, were considered to be observed and used in the structure refinement. The intensities were corrected for Lorentz-polarization effects but not for absorption. The linear absorption coefficient of the compound was found to be 13.5 cm^{-1}.

Solution and refinement of the structure. The positions of the ruthenium and phosphorus atoms were obtained from a three-dimensional Patterson synthesis. A cycle of full-matrix least-squares refinement and a difference Fourier synthesis revealed the remaining non-hydrogen atoms. Two of the O—CH_3 groups were found to be disordered. In each case there were two conformations with distinct oxygen atom positions (~1 Å apart) and superimposed methyl carbon atom positions. A three-dimensional difference synthesis based on a model with the disordered O—CH_3 atoms omitted indicated approximately equal populations for the disordered positions. For these two O—CH_3 groups, two oxygen atoms with site occupancies of 0.5 were used for each group. Further full-matrix least-squares refinement with anisotropic thermal parameters for the non-disordered atoms followed by a three-dimensional difference Fourier synthesis revealed the methyl hydrogen atoms on the ordered P—O—CH_3 arm. The hydrogen atoms were included in fixed positions with temperature factors equal to the carbon atom to which they were bonded. An examination of the strong low-angle data showed $|F_o|$ to be lower than $|F_c|$ and on the assumption that this indicated extinction, refinement of an extinction coefficient was included. Refinement converged with final factors $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.044$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2} = 0.058$. The final value for the extinction coefficient was 3.7(3) × 10^{-7}. No parameter shifted by more than σ on the final cycle of least-squares refinement. Peaks up to 0.97 eÅ^{-3} (~6σ) were found on the final difference Fourier map near the

TABLE 1

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^2$) FOR $Ru(CO)_4[P(OCH_3)_3]$ [a]

Atom	x	y	z	U
Ru	0.20411(3)	0.03724(5)	0.01060(3)	[b]
P	0.3189(1)	0.2534(2)	0.1037(1)	[b]
O(1)	0.3860(4)	−0.1066(8)	−0.0583(5)	[b]
O(2)	0.1840(6)	−0.0834(9)	0.2220(4)	[b]
O(3)	0.0457(4)	0.3102(8)	−0.1230(5)	[b]
O(4)	0.0606(4)	−0.2626(8)	−0.1087(4)	[b]
O(5)	0.4189(3)	0.1797(5)	0.1906(3)	[b]
C(1)	0.3192(5)	−0.0540(7)	−0.0320(5)	[b]
C(2)	0.1927(6)	−0.0401(8)	0.1445(5)	[b]
C(3)	0.1046(5)	0.2102(8)	−0.0732(5)	[b]
C(4)	0.1129(5)	−0.1509(8)	−0.0657(5)	[b]
C(5)	0.5071(5)	0.2840(8)	0.2567(5)	[b]
C(6)	0.1878(6)	0.4502(9)	0.1690(6)	94(2)
C(7)	0.3598(7)	0.4073(12)	−0.0578(7)	108(2)
O(6A) [c]	0.2824(5)	0.3578(8)	0.1959(5)	59(2)
O(6B) [c]	0.2763(7)	0.4288(11)	0.1277(7)	81(2)
O(7A) [c]	0.3440(6)	0.4130(10)	0.0493(5)	65(2)
O(7B) [c]	0.3968(6)	0.3442(10)	0.0399(5)	73(2)
H(1)	0.506	0.392	0.263	90
H(2)	0.569	0.266	0.235	90
H(3)	0.527	0.244	0.330	90

[a] The estimated standard deviation is given in parentheses in this and the following tables. [b] See Table 2 for anisotropic thermal parameters. [c] Disordered atom with a population parameter of 0.5.

disordered atoms. Although the model does not fully describe the disorder it was not considered worthwhile pursuing further. The least-squares refinement was based on minimization of the function $\Sigma w(|F_o| - |F_c|/1 + E_c I_o)^2$ *. A weighting scheme of the type $w = 1/\sigma(F_o)^2$ was used in the final stages of refinement. Atomic scattering factors for all non-hydrogen atoms, including anomalous dispersion corrections for ruthenium were taken from ref. 8 while those for hydrogen from ref. 9. The computer programs used in the structure determination and refinement have been noted elsewhere [10].

The final positional and thermal parameters are given in Tables 1 and 2, respectively. Bond distances and angles, with estimated standard deviations calculated from the inverse matrix, are given in Tables 3 and 4. Two views of the molecule with the atomic numbering scheme are shown in Figures 1 and 2. An abnormally short distance between the non-bonded O(6B) and O(7A) atoms indicated that they be numbered as belonging to different conformers of the phosphite ligand **.

Results and discussion

Two convenient routes to $Ru(CO)_4[P(OCH_3)_3]$ have been found. The first method involved the initial conversion of $Ru_3(CO)_{12}$ to $Ru(CO)_5$ and subse-

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* Where E_c is the extinction coefficient and I_0 the net measured intensity.

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TABLE 2

ANISOTROPIC THERMAL PARAMETERS (Å^2 X 10^3) FOR $Ru(CO)_4[P(OCH_3)_3]$

Atom	U_{11} [a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	51.1(3)	52.3(4)	54.7(3)	−5.9(2)	−14.0(2)	−6.9(2)
P	56.8(7)	44.0(6)	60.7(7)	−1.4(5)	10.5(5)	−1.8(5)
O(1)	90(3)	120(4)	143(4)	15(3)	50(3)	−37(4)
O(2)	207(6)	129(4)	79(3)	−78(5)	56(4)	−9(3)
O(3)	97(3)	105(4)	128(4)	26(3)	−16(3)	12(3)
O(4)	110(4)	122(4)	126(4)	−51(3)	40(3)	−58(4)
O(5)	74(2)	56(2)	88(2)	−11(2)	−14(2)	4(2)
C(1)	67(3)	66(4)	79(3)	0(3)	18(3)	−10(3)
C(2)	112(5)	70(4)	73(4)	−38(3)	32(3)	−9(3)
C(3)	66(3)	78(4)	83(4)	−5(3)	6(3)	−5(3)
C(4)	74(3)	77(4)	84(3)	−19(3)	27(3)	−24(3)
C(5)	85(4)	76(4)	102(5)	−25(3)	−10(3)	−6(4)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)]$

quent reaction of the $Ru(CO)_5$ with $P(OCH_3)_3$ at room temperature. The second route employed the direct reaction of $Ru_3(CO)_{12}$ and $P(OCH_3)_3$ in hexane solution at 125°C under 80 atmospheres of carbon monoxide. This latter method has proved suitable for the preparation of similar derivatives (e.g., $Ru(CO)_4(PPh_3)$) but not for others (e.g., $Ru(CO)_4[P(o\text{-tolyl})_3]$).

It was also noted that $Ru_3(CO)_{12}$ reacts with a large excess of $P(OCH_3)_3$, in hexane solution, to give, with traces of a third product, a mixture of $Ru(CO)_4[P(OCH_3)_3]$ and $Ru(CO)_3[P(OCH_3)_3]_2$ in a ratio of approximately 2 : 1. This is similar to the observations of Poë and coworkers concerning the reaction of P(n-butyl)$_3$ with $Ru_3(CO)_{12}$ [11].

Crystal structure of $Ru(CO)_4[P(OCH_3)_3]$

The crystal structure of $Ru(CO)_4[P(OCH_3)_3]$ reveals that the coordination

TABLE 3

BOND DISTANCES (Å) FOR $Ru(CO)_4[P(OCH_3)_3]$

Ru—P	2.309(2)
Ru—C(1)	1.928(7)
Ru—C(2)	1.929(7)
Ru—C(3)	1.937(6)
Ru—C(4)	1.938(6)
C(1)—O(1)	1.129(8)
C(2)—O(2)	1.125(8)
C(3)—O(3)	1.135(7)
C(4)—O(4)	1.130(7)
P—O(5)	1.539(4)
P—O(6A)	1.667(6)
P—O(6B)	1.538(9)
P—O(7A)	1.519(7)
P—O(7B)	1.692(8)
O(5)—C(5)	1.443(6)
O(6A)—C(6)	1.377(7)
O(6B)—C(6)	1.460(11)
O(7A)—C(7)	1.507(11)
O(7B)—C(7)	1.315(10)

TABLE 4

BOND ANGLES (deg) FOR $Ru(CO)_4[P(OCH_3)_3]$

P—Ru—C(4)	177.6(2)
P—Ru—C(1)	88.8(2)
P—Ru—C(2)	88.4(2)
P—Ru—C(3)	90.4(2)
C(1)—Ru—C(2)	118.3(3)
C(1)—Ru—C(3)	122.2(3)
C(2)—Ru—C(3)	119.5(3)
C(1)—Ru—C(4)	89.3(2)
C(2)—Ru—C(4)	91.2(2)
C(3)—Ru—C(4)	91.9(3)
Ru—C(1)—O(1)	179.0(9)
Ru—C(2)—O(2)	178.6(14)
Ru—C(3)—O(3)	179.3(10)
Ru—C(4)—O(4)	178.8(7)
Ru—P—O(5)	112.1(2)
Ru—P—O(6A)	116.1(2)
Ru—P—O(6B)	121.6(3)
Ru—P—O(7A)	122.7(3)
Ru—P—O(7B)	115.6(3)
O(5)—P—O(6A)	91.0(3)
O(5)—P—O(6B)	116.8(4)
O(5)—P—O(7A)	112.6(3)
O(5)—P—O(7B)	90.8(3)
O(6A)—P—O(7A)	97.1(4)
O(6B)—P—O(7B)	93.9(4)
P—O(5)—C(5)	124.2(4)
P—O(6A)—C(6)	121.5(5)
P—O(6B)—C(6)	125.0(7)
P—O(7A)—C(7)	123.2(6)
P—O(7B)—C(7)	124.1(7)

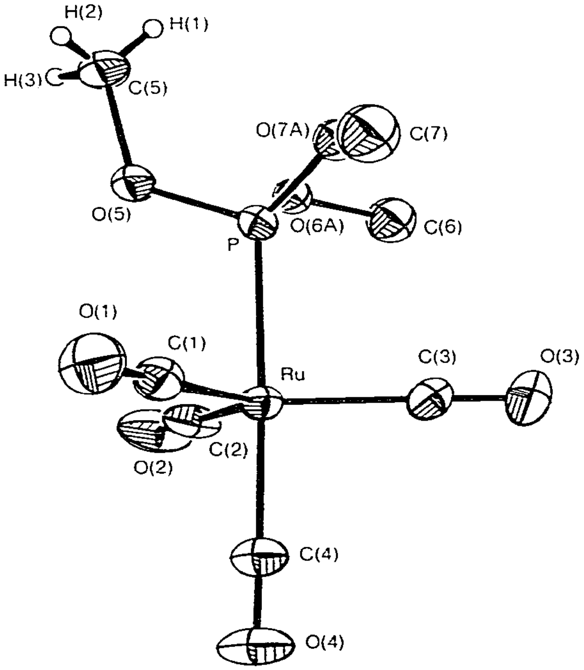

Fig. 1. The molecular structure of $Ru(CO)_4[P(OCH_3)_3]$.

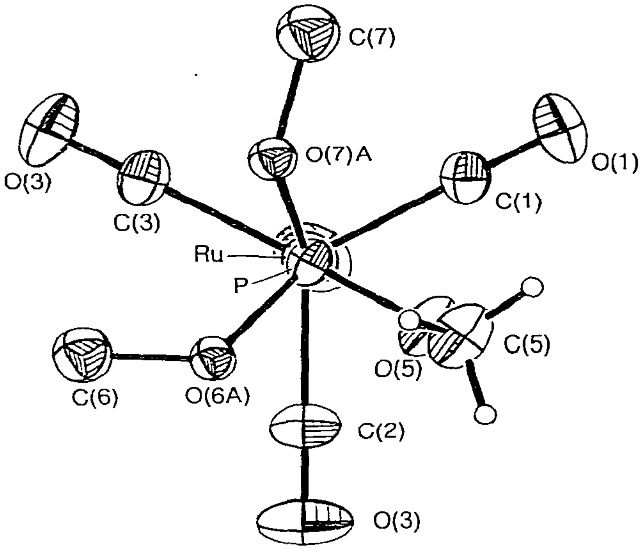

Fig. 2. View of the molecule down the P—Ru axis.

about the ruthenium atom is close to trigonal bipyramidal with the phosphite ligand in the axial position (Figure 1). The present structure may be compared to that recently reported for $Ru(CO)_4(SbPh_3)$ in which the coordination about the central ruthenium atom was distorted trigonal bipyramidal with the $SbPh_3$ group in an equatorial position [12].

It is of interest that the Ru—C distance (Table 1) *trans* to $P(OCH_3)_3$ is not significantly shorter than the metal—carbon distances in the equatorial plane. This is in contrast to the bond lengths found for the octahedral molecule $Cr(CO)_5[P(OPh)_3]$ where the Cr—C distance *trans* to the phosphite ligand was shorter than the other Cr—C distances [13].

The structure determination suffered because of disorder in two of the $O—CH_3$ arms of the phosphite ligand. This appears to be a common problem for structures containing the $P(OCH_3)_3$ group, especially when the structure is determined near room temperature [14—18]. The P—O and O—C distances are widely different, long P—O distances are associated with short O—C distances and vice versa. These differences, which again are typical of structures with disordered $P(OCH_3)_3$ ligands, are almost certainly due to the failure to accurately describe the disorder in the structural analysis rather than any exceptional electronic effect. The analogous distances found for $HFeCo_3(CO)_9[P(OCH_3)_3]_3$, where disorder was not a problem *, do not show the same wide variation [17]. The average P—O (1.594(8) Å) and O—C (1.438(4) Å) distances found for $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ are in good agreement with the corresponding distances observed for the non-disordered $P—O—CH_3$ linkage in $Ru(CO)_4[P(OCH_3)_3]$.

The present structure, however, clearly shows that the trimethyl phosphite

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* The structure of this compound was determined by neutron diffraction techniques at 90°K. Two of the $P(OCH_3)_3$ groups have the same conformation as that found for the trimethyl phosphite ligand in the present structure.

ligand lacks three-fold symmetry with two of the methyl groups pointing down (at an angle) from the plane of oxygen atoms, whereas the third methyl group points almost directly up from the plane. The molecule (including disorder) has close to mirror symmetry. However, from the non-bonded contacts, it is concluded that each individual phosphite ligand is comprised of one pair of non-mirror related disordered oxygen atoms. Hence, each individual molecule would not have mirror symmetry. It should also be noted that the P—O directions are staggered with respect to the Ru—C bonds (Fig. 2).

An examination of other structures containing the $P(OCH_3)_3$ ligand suggests this is the most common orientation of the methyl groups (Table 5). Only in crowded molecules such as $Ni[P(OCH_3)_3]_4Br$ do the $P(OCH_3)_3$ ligands adopt different conformations and this can probably be attributed to steric interactions. Even in these cases (with one exception) there is one methyl group which points directly up out of the oxygen plane. That a wide range of different $P(OCH_3)_3$ complexes have the "two down, one up" arrangement of methyl groups suggests it is a property of the ligand and not a configuration induced by the environment. Although this asymmetry has been briefly mentioned before [22] it does not appear to be appreciated in the literature. The reasons

TABLE 5

DISTANCES OF THE METHYL CARBONS FROM THE OXYGEN PLANE IN $P(OCH_3)_3$ LIGANDS [a] ($L = P(OCH_3)_3$)

Compound	C_1	C_2	C_3	Ref.
$Ru(CO)_4L$	−0.30	−0.43	+1.43	b
$Ru(CO)_4L$	−0.31	−0.38	+1.43	b
$[Co(CNC_6H_4F)_3L_2]BF_4$	−0.33	−0.46	+1.48	19
$(C_5H_5)Mo(CO)_2LI$	−0.31	−0.32	+1.52	20
$(CH_3C_5H_4)Mo(CO)_2LI$	−0.30	−0.35	+1.46	20
$[AgL_2(NO_3)]_2$	−0.30	−0.35	+1.53	21
$[AgL_2(NO_3)]_2$	−0.54	−0.55	+1.49	21
$(C_5H_5)Mo[CC(CN)_2]L_2Cl$	−0.28	−0.33	+1.43	14
$Fe(CO)_3L_2$	−0.28	−0.36	+1.45	22
$W_2H(CO)_8(NO)L$	−0.18	−0.25	+1.49	16
$Mo(CO)_4(NHC_5H_{10})L$	−0.30	−0.38	+1.48	23
$(C_4H_7)_2RuL_2$	−0.19	−0.33	+1.49	24
$(C_4H_7)_2RuL_2$	−0.18	−0.28	+1.38	24
$[Ir(\mu\text{-}SR)(CO)L]_2$	−0.15	−0.36	+1.49	25
$[Ir(\mu\text{-}SR)(CO)L]_2$	−0.39	+0.32	+1.50	25
$[Ir(H)(\mu\text{-}SR)(CO)L]_2$	−0.29	−0.31	+1.46	25
$\{L(OC)_2Co[(CH_2)_2CCH_2]\}_2CO$	−0.39	−0.41	+1.38	18
$\{L(OC)_2Co[(CH_2)_2CCH_2]\}_2CO$	−0.34	−0.55	+1.43	18
$HFeCo_3(CO)_9L_3$	−0.01	−0.36	+1.44	26
$HFeCo_3(CO)_9L_3$	−0.03	−0.35	+1.44	26
$HFeCo_3(CO)_9L_3$	−0.35	+1.20	+1.41	26
NiL_3I_2	−0.20	−0.43	+1.46	27
MiL_3I_2	−0.22	+0.83	+1.46	27
NiL_3I_2	−0.41	+0.45	+1.43	27
NiL_4Br	−0.12	+1.08	+1.41	28
NiL_4Br	−0.22	+0.03	+1.47	28
NiL_4Br	−0.44	+0.21	+1.45	28
NiL_4Br	−0.88	+1.04	+1.20	28

[a] The side of the plane opposite the phosphorus is taken as positive. [b] The first line refers to the A set of the disordered oxygen atoms, the second the B set (of this work).

for adoption of this conformation are not clear. Hardy and Sim have suggested [20] that the P—O bonds have some double-bond character and recent molecular orbital calculations [27] on $P(OCH_2)_3CCH_3$ indicated that such O(2*p*)—P(3*d*) interactions are important. It is interesting to speculate that the configuration found here maximizes these interactions while keeping interligand repulsions to a minimum.

Spectroscopic studies

The infrared spectrum of $Ru(CO)_4[P(OCH_3)_3]$ in the carbonyl region shows four sharp carbonyl stretches (Figure 3). This differs from three expected for a trigonal bipyramidal molecule of the type $M(CO)_4L$ with L axial (C_{3v} symmetry) [30,31]. Other carbonyl complexes containing the $P(OCH_3)_3$ group often exhibit more CO stretches than would be expected if the phosphite ligand had three-fold symmetry [32].

The $P(OC_2H_5)_3$ analogue $Ru(CO)_4[P(OC_2H_5)_3]$ also shows a splitting of the lowest energy carbonyl band. However, the $P(OCH_2)_3CC_2H_5$ derivative, in which the P—O—C skeleton is held rigid, does not show this splitting. The band is also much more intense (Figure 4). This suggests that the asymmetry found in the solid state is also maintained, on the infrared time scale, in solution. The presence of conformers would be expected to cause doubling or at least a

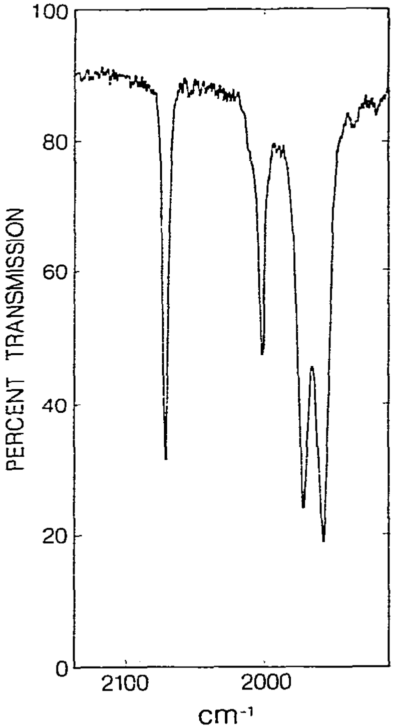

Fig. 3. Carbonyl stretching region of the infrared spectrum of $Ru(CO)_4[P(OCH_3)_3]$ in hexane solution.

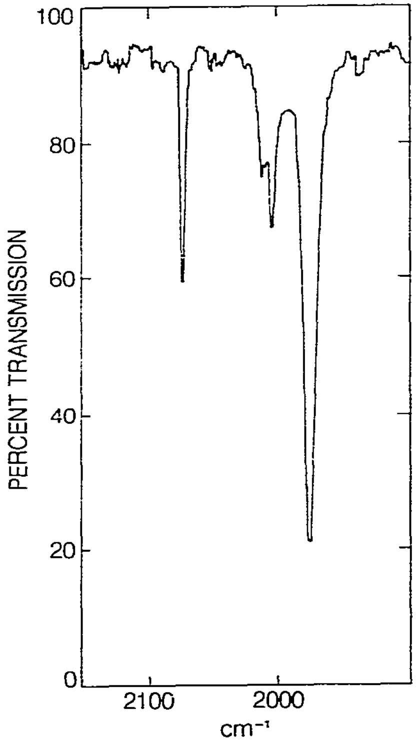

Fig. 4. Carbonyl stretching region of the infrared spectrum of $Ru(CO)_4[P(OCH_2)_3CC_2H_5]$ in hexane solution.

broadening of all three carbonyl bands [33]. Significant amounts of the equatorial isomer would also be expected to cause the appearance of additional carbonyl bands [34].

Of interest is the fact that the low energy carbonyl band of $Ru(CO)_4(PPh_2CH_3)$ is only slightly broader than that in $Ru(CO)_4PPh_3$; both compounds exhibit only three infrared active carbonyl stretches even though the former molecule has only C_s symmetry.

The ^1H and ^{13}C NMR spectra of $Ru(CO)_4[P(OCH_3)_3]$ in CCl_2FH at —120°C indicate the methyl groups are all equivalent, i.e., there is rapid interconversion of the two types of methyl group on the NMR time scale. The ^{13}C NMR spectrum (at —120° C) also revealed only one signal (coupled to ^{31}P) due to the carbonyl groups. As has been observed previously for $Fe(CO)_4L$ compounds [31,34,35], the axial and equatorial carbonyl groups undergo rapid exchange in solution.

From Figure 4 it is seen that $Ru(CO)_4[P(OCH_2)_3CC_2H_5]$ does exhibit a fourth weak carbonyl stretch (at 2012 cm^{-1}) besides the three principal absorptions. This peak remained unchanged in intensity after recrystallization and sublimation of the compound, suggesting that it is not due to an impurity. It may indicate the presence of a small amount of the isomer having the phosphite in an equatorial position. The PF_3 analogue exhibits more than three carbonyl absorptions, suggesting significant concentrations of both the axial and equatorial isomers [36]. Also $Ru(CO)_4(SbPh_3)$, in which the $SbPh_3$ group adopts an equatorial position in the solid state, shows at least five infrared active carbonyl absorptions in solution [12]. Note that the rearrangement of the axial and equatorial carbonyl groups by the Berry mechanism [37] would necessarily involve an intermediate with the phosphite ligand in the equatorial position.

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