Experimental Section

The infrared spectrum was recorded on a Perkin-Elmer 521 spectrometer. NMR spectra were recorded at 15.08 MHz in the Fourier transform mode on a Bruker WP60 spectrometer. All reported shifts are downfield relative to tetramethylsilane. The mass spectrum were measured on an AEI MS-9 high-resolution mass spectrometer with a DS-30 data system. An ionizing voltage of 70 eV was used. Reagents obtained from the indicated sources were used without further purification: hexaethylbenzene, $Cr(CO)_6$ (Pfaltz & Bauer); PEt_3 (Fluka).

Tricarbonyl(hexaethylbenzene)chromium(0) (3) was prepared as described previously.[2]

Dicarbonyl(hexaethylbenzene)(triethylphosphine)chromium(0) (1) was prepared by UV irradiation for 1 h of a freeze–thaw degassed pentane (30 ml) solution of **3** (0.18 g, 0.47 mmol) and PEt_3 (0.1 g, 0.68 mmol) contained in a quartz vessel. The pentane solution was filtered under a nitrogen atmosphere and the solvent removed. The solid residue was recrystallized from pentane to give orange crystals of **1**: IR (KBr) 1789, 1846, 1857, 1948 cm^{-1}; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ambient temperature) δ 6.5, 15.2, 16.1, 21.2, 22.5 (ethyl),[18] 106.9 (C_{ar}), 244.3 (CO, $^2J_{PC}$ = 22 Hz); mass spectrum, m/e (relative intensity) 472 (M^+, 8), 416 ($M^+ - 2CO$, 45), 326 ($M^+ - CO - PEt_3$, 7), 298 ($M^+ - 2CO - PEt_3$, 57), 246 ($M^+ - 2CO - PEt_3 - Cr$, 100); mass spectrum (high resolution), m/e 472.2560 (472.2562 calcd for $C_{26}H_{45}{}^{52}CrO_2P$).

Crystallography. Crystals of **1**, obtained by slow evaporation of a pentane solution, are monoclinic: $P2_1/c$; a = 9.729 (4) Å, b

$= 18.353$ (6) Å, c = 29.869 (12) Å, β = 98.26 (2)°; d_{calcd} = 1.189 g cm^{-3} for Z = 8 ($C_{26}H_{45}CrO_2P$, mol wt 472.61). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse–height discrimination). The size of the crystal used for data collection was approximately 0.15 $\times$ 0.15 $\times$ 0.5 mm; the data were corrected for absorption (μ = 44.4 cm^{-1}). A total of 4951 independent reflections were measured for $\theta < 48°$, of which 4015 were considered to be observed ($I > 2.5\sigma(I)$). The structure was solved by the heavy-atom method after the positions of the four chromium and phosphorus atoms had been obtained from an E map. A block-diagonal least-squares, in which the matrix was partitioned into two blocks, was used for the final refinement. Two reflections which were strongly affected by extinction were excluded from the final refinement and difference map. Anisotropic thermal parameters were used for nonhydrogen atoms and isotropic temperature factors were used for hydrogen atoms in the final refinement. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are $R = 0.041$ and $R_w = 0.044$ for the 4013 observed reflections. The final difference map has no peaks greater than ± 0.5 e Å^{-3}.

Supplementary Material Available: Final anisotropic thermal parameters and atomic parameters for hydrogen atoms, with standard deviations for 1A and 1B and a structure factor table for 1 (20 pages). Ordering information is given on any current masthead page.

(17) Crystal packing effects are also unlikely to play a significant role in determining the conformations of 1 and 2, since there are no intermolecular H···H contacts shorter than 2.3 Å.

(18) Absorptions from the ethyl groups of HEB overlap with those of triethylphosphine, and no attempt was made to assign individual CH$_3$ and CH$_2$ signals.

The Series Ru(CO)$_{5-n}$[P(OMe)$_3$]$_n$ (n = 1–5). Methyl Migration in Ru[P(OMe)$_3$]$_5$

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Pentakis(trimethyl phosphite)ruthenium, Ru[P(OMe)$_3$]$_5$ (**5**), has been prepared by the ultraviolet irradiation of a hexane solution of Ru$_3$(CO)$_{12}$ and excess P(OMe)$_3$. When the reaction was followed by ^{31}P$\{^1$H$\}$ NMR spectroscopy, the stepwise formation of Ru(CO)$_{5-n}$[P(OMe)$_3$]$_n$ (n = 1–5) was indicated. Alternative syntheses for the derivatives with n = 1–4 are reported. As previously found for Ru(CO)$_4$[P(OMe)$_3$], Ru(CO)$_{5-n}$[P(OMe)$_3$]$_n$ (n = 3, 4) are probably fluxional, on the NMR time scale, in solution. When **5**, in hexane solution, was heated to 120 °C, it isomerized to Ru[P(OMe)$_3$]$_4$(CH$_3$)[P(O)(OMe)$_2$] (**5i**). Treatment of either **5** or **5i** with MeI gave {Ru[P(OMe)$_3$]$_5$(CH$_3$)}I. The preparation of the ortho-metalated compound, (H)$\overline{\text{Ru}[(C_6H_4O)P(OPh)_2]}$[P(OMe)$_3$]$_3$, from Ru(CO)$_2$[P(OMe)$_3$]$_3$ and P(OPh)$_3$ is also described.

Introduction

In the past several years it has become apparent that phosphites, and trimethyl phosphite in particular, are able to stabilize transition metals in low, or formally zero, oxidation states. These complexes (e.g., Cr[P(OMe)$_3$]$_6$,[1] W[P(OMe)$_3$]$_6$,[2] Co[P(OPh)$_3$]$_4$H[3]) have stoichiometries that resemble the corresponding carbonyl derivatives. However, due to the different electronic and steric properties of the CO and P(OR)$_3$ ligands, it would be expected that the two

types of compounds would have different chemical properties.

Two groups have reported the synthesis of Fe[P(OMe)$_3$]$_5$ and described aspects of its chemistry.[4,5] The preparation of the ruthenium analogue, Ru[P(OMe)$_3$]$_5$ (**5**), has also been mentioned together with its temperature-dependent ^{31}P$\{^1$H$\}$ NMR spectrum.[6] The preparation involved the sodium amalgam reduction of Ru[P(OMe)$_3$]$_4$Cl$_2$ in the

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presence of excess trimethyl phosphite. During our study[7] of the preparation of some $Ru(CO)_4L$ derivatives, it was noted that 5 could be prepared by the ultraviolet irradiation of a hexane solution of $Ru_3(CO)_{12}$ and excess P-$(OMe)_3$. This method is similar to that used by Mathieu and Poilblanc[8] to prepare $Mo[P(OMe)_3]_6$, although it does not appear to have been exploited since this original report.

In this paper we describe the details of the preparation of $Ru[P(OMe)_3]_5$ using this method, along with the synthesis of the other members of the series $Ru(CO)_{5-n}[P-(OMe)_3]_n$ ($n = 1$–5). The isomerization of 5 to $Ru[P-(OMe)_3]_4(Me)[P(O)(OMe)_2]$ is also reported. This work has been the subject of a preliminary communication.[9]

Experimental Section

General Procedure. Unless otherwise stated, reactions (and the purification of solvents) were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Hexane was refluxed over potassium, distilled, and stored over type 4A molecular sieves before use. Dodecacarbonyltriruthenium was prepared by a literature method.[10] Trimethyl phosphite, as obtained commercially, was transferred under nitrogen to a 500-mL round-bottom flask fitted with a Teflon valve and stored under nitrogen before use; it was pure by $^{31}P\{^1H\}$ NMR spectroscopy. Previously, impure trimethyl phosphite was purified by distillation from sodium (under nitrogen). The ultraviolet irradiations were carried out with use of a Hanovia 200-W lamp inside a water-cooled, quartz jacket. The reactants were contained in thick-walled Pyrex, Carius tubes (30 cm × 3 cm diameter) fitted at one end with a Teflon valve. There was approximately 3 cm between the edge of the UV source and the edge of the solution. Infrared spectra were recorded with a Perkin-Elmer 237 spectrometer fitted with an external recorder. The spectra (carbonyl region) were calibrated by using carbon monoxide. Phosphorus NMR spectra were obtained on a Varian XL 100 instrument (operating in the Fourier transform mode, with proton decoupling). An internal reference of $P(OMe)_3$ was used, and the chemical shifts referred to H_3PO_4 (δ 0, downfield negative) by taking the ^{31}P resonance of trimethyl phosphite (in hexane, ambient temperature) as -140.5 ppm. Proton NMR spectra were obtained on the same instrument with the exception of the spectrum of $Ru[P-(OMe)_3]_4(CH_3)[P(O)(OMe)_2]$ shown in Figure 2. This spectrum was obtained on the Bruker 400-MHz instrument at the University of Alberta; the spectrum was recorded with the phosphorus nuclei partially decoupled. Mass spectra were obtained on a Hewlett-Packard 5985 GC-MS system with an ionization voltage of 80 eV except in the cases of $Ru[P(OMe)_3]_5$ and $Ru[P(OMe)_3]_4(CH_3)-[P(O)(OMe)_2]_2$ where chemical ionization (with CH_5^+) was used. Microanalyses were performed by Mr. M. K. Yang of the microanalytical laboratory of Simon Fraser University or by Canadian Microanalytical Service Ltd., Vancouver, B.C. Melting points were measured in sealed capillaries under nitrogen on a Gallenkamp apparatus.

$Ru(CO)_4[P(OMe)_3]$ and $Ru(CO)_3[P(OMe)_3]_2$. A glass Carius tube containing $Ru_3(CO)_{12}$ (0.32 g, 0.50 mmol) and $P(OMe)_3$ (2.5 mL, 21 mmol) in hexane (20 mL) was cooled to -196 °C and evacuated; the solution was degassed with two freeze–thaw cycles. The solution was stirred at room temperature for 24 h. An infrared spectrum (carbonyl region), after this period, of the orange-red solution indicated the presence of $Ru(CO)_4[P(OMe)_3]$ (1) and $Ru(CO)_3[P(OMe)_3]_2$ (2) in an approximate 2:1 ratio. There were also other absorptions of weak intensity which indicated the presence of other ruthenium–carbonyl species. An infrared spectrum of a reaction solution which had been stirred for a further 96 h revealed a slight decrease in the intensity of the bands due to 1, with a corresponding increase in those due to 2. The solution was also a much paler red color.

The monosubstituted complex, 1, may be separated from 2 by fractional sublimation at $<5 \times 10^{-3}$ mm and 0 °C, to a probe at -78 °C. After the removal of 1, which takes approximately 72 h, 2 may be obtained by vacuum sublimation at 40 °C (to a probe at -78 °C). The yields of 1 and 2, as isolated by this method, were 58% and 35%, respectively. A faster method of separation was by column chromatography on Florisil. The Florisil was previously heated to 130 °C under vacuum for 72 h, deactivated by slurrying with anhydrous diethyl ether/hexane (1:4, by volume), and finally washed free of the excess ether with hexane. The hexane and excess $P(OMe)_3$ from the reaction solution were removed on the vacuum line, and the resulting solid was dissolved in hexane (5 mL). This solution was placed on the column (25 × 1.5 cm) and eluted with hexane to give 1 (0.13 g, 26%). Further elution with hexane/toluene (1:1, by volume) afforded 2 (0.15 g, 23%). Subsequent elution using pure toluene yielded a small amount of a red-orange, crystalline solid which was identified as $Ru_3-(CO)_9[P(OMe)_3]_3$. (Anal. Calcd for $C_{18}H_{27}O_{18}P_3Ru_3$: C, 23.30; H, 2.93. Found: C, 23.24;, H, 2.93. $\nu(CO)$: 2058 (vw), 2000 (sh), 1989 (s), 1962 (sh); lit.[11] 2054 (w), 2001 (sh), 1988 (s), 1963 (s).) There was evidence for traces of at least two other products on the column which have not been identified. (From the yields obtained by the use of sublimation to effect separation, it is evident that much of 1 and 2 were retained on the column.)

Although the colorless crystals of 1 can be handled for very short periods in air, it appeared to be both thermally, and photochemically, unstable. It could be stored at -15 °C in the dark for long periods without apparent decomposition. It may be recrystallized from hexane at -78 °C. The bis(phosphite) derivative, 2, is likewise a colorless solid which becomes yellow on prolonged exposure to air and light, although it is more robust than 1. It may be recrystallized from hexane at -15 °C.

$Ru(CO)_2[P(OMe)_3]_3$ (3). A glass Carius tube containing $Ru_3(CO)_{12}$ (0.32 g, 0.50 mmol) and $P(OMe)_3$ (2.5 mL, 21 mmol) in hexane (15 mL) was evacuated at -196 °C and the solution degassed with two freeze–thaw cycles. The tube was heated at 100 °C for 72 h; the evolved carbon monoxide was removed, at -196 °C, at 12-h intervals. Hexane and excess trimethyl phosphite were removed under vacuum from the resultant yellow solution. To remove occluded $P(OMe)_3$, the remaining yellow solid was redissolved in hexane (5 mL) and again evaporated to dryness on the vacuum line to give $Ru(CO)_2[P(OMe)_3]_3$ (0.74 g, 93%). The sample was recrystallized from hexane, at -15 °C, to give pale yellow, almost colorless, needles.

The tris(phosphite) complex is stable for short periods in air, although it does decompose on prolonged exposure. It is indefinitely stable under nitrogen or vacuum at room temperature.

When the reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy, a spectrum after 72 h showed only the presence of 3 and $P(OMe)_3$. However, in a reaction of $Ru_3(CO)_{12}$ with $P(OMe)_3$ in hexane at 135 °C, a small quantity of $Ru(CO)[P(OMe)_3]_4$ was detected in the solution after 7 days.

$Ru(CO)[P(OMe)_3]_4$ (4). A glass Carius tube with $Ru[P-(OMe)_3]_5$ (0.99 g, 1.37 mmol) in hexane (15 mL) was evacuated and the solution degassed as before. The tube was then pressurized with carbon monoxide (2 atm) and the stirred solution irradiated with UV light for 1.5 h. A $^{31}P\{^1H\}$ NMR spectrum of the solution at this stage showed, besides free $P(OMe)_3$, $Ru-(CO)_2[P(OMe)_3]_3$, and $Ru(CO)[P(OMe)_3]_4$ in a ratio of approximately 1:20, plus traces of $Ru[P(OMe)_3]_5$. The hexane and $P(OMe)_3$ were removed on the vacuum line to leave a sticky yellow solid (yield 0.86 g, $\sim$100%). Most of 3, plus some 4, was removed by sublimation (for 10 h), at 75 °C and $<5 \times 10^{-3}$ mm, onto a water-cooled probe (9 °C). The remaining yellow solid was recrystallized from hexane three times to give 4 as pale yellow, waxy crystals which were analytically pure. The compound can be handled for short periods in air but does decompose on prolonged exposure.

The tetrasubstituted derivative, 4, was also detected by $^{31}P\{^1H\}$ NMR spectroscopy during the preparation of $Ru[P(OMe)_3]_5$ (5): the maximum concentration of 4 occurred after approximately 24-h irradiation. It was also the major product when 5 was treated in hexane with carbon monoxide (85 atm) at 75 °C for 12 h. There

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was some unreacted starting material, and **3**, also present in this reaction. If desired **4** may be separated from **3** and **5** by column chromatography on Florisil deactivated with P(OMe)₃ (see below).

Ru[P(OMe)₃]₅ (5). A glass Carius tube with Ru₃(CO)₁₂ (0.41 g, 0.64 mmol) and P(OMe)₃ (8 mL, 68 mmol) in hexane (20 mL) was evacuated and the solution degassed, as previously described. The stirred solution was then irradiated with UV light for approximately 48 h. The evolved carbon monoxide was removed from the reaction vessel after 4, 8, 20, and 36 h. After the irradiation, the very pale yellow solution was transferred to a Schlenk flask and cooled to -78 °C for 6 h. The colorless supernatant liquid was separated from an oily yellow precipitate by transferring it to a second Schlenk flask. All volatiles were removed from the supernatant solution on the vacuum line to give **5** (0.67 g, 48%) as a white, waxy, crystalline solid. The purity of the product was estimated at >99% by ³¹P{¹H} NMR spectroscopy. (The yellow oil described above contained significant amounts of **5**.)

Two other methods of isolation of **5** were attempted. In the first method the volatiles from the reaction solution were removed on the vacuum line, and the resultant yellow waxy solid was extracted with hexane (3 × 5 mL). The extracts were then chromatographed on Florisil (1.25 × 8 cm column, eluant hexane). The florisil had previously been heated at 130 °C under vacuum for 72 h and then deactivated by slurrying with a 1:1 hexane-trimethyl phosphite solution. The product isolated by this method was in lower yield (34%) and less pure by ³¹P{¹H} NMR spectroscopy: it contained up to 10% of **4** and other products. It appeared that significant amounts of **5** were retained on the column. In the second method the solid from the reaction solution, after removal of the volatiles, was extracted with hexane (3 × 10 mL). The extracts were filtered through 1 cm of neutral grade alumina (activity 1).⁶ The final extract was eluted from the alumina with hexane (8 mL). The extracts were combined, and the solvent was removed on the vacuum line to give **5** (yield 65%). The purity of the product as isolated by this method was estimated to be at least 98% (by ³¹P{¹H} NMR spectroscopy).

The time at which optimum yields of **5** are obtained for a particular UV source and glass tube are best determined by monitoring the reaction by ³¹P{¹H} NMR spectroscopy. Prolonged irradiation of the solution causes further reaction of **5** as evidenced by a number of multiplets in the ³¹P{¹H} NMR spectrum.

Ru[P(OMe)₃]₄(CH₃)[P(O)(OMe)₂] (5i). A glass Carius tube containing Ru[P(OMe)₃]₅ (0.30 g, 0.42 mmol) in hexane (20 mL) was evacuated and degassed as before. The tube was then heated for 24 h at 120 °C. A ³¹P{¹H} NMR spectrum of the solution at this stage indicated complete reaction of **5**, with **5i** the sole product. The colorless solution was transferred to a Schlenk flask and cooled to -78 °C for several hours, whereupon a white precipitate formed. The supernatant liquid was removed from the precipitate which was then dried on the vacuum line. Recrystallization of the white precipitate from hexane gave Ru[P(OMe)₃]₄(CH₃)[P(O)(OMe)₂] as colorless plates.

Some factors which influenced the rate of isomerization of **5** were studied by using ³¹P{¹H} NMR spectroscopy. The reactions were carried out in 12-mm NMR tubes fitted with a Teflon valve so that they could be evacuated on the vacuum line and sealed. In one experiment, two identical tubes were each charged with **5** (0.27 g, 0.37 mmol) and hexane (4.5 mL). To one tube was added P(OMe)₃ (0.10 mL, 0.85 mmol). Both tubes were then evacuated and the solutions degassed as before and placed in an oil bath at 110 °C. The extent of isomerization was monitored by ³¹P{¹H} NMR at approximately 1-h intervals. After 5 h, the solution with the added P(OMe)₃ showed virtually no isomerization of **5** whereas it was approximately 50% complete in the other reaction. In a second experiment one tube was charged with 0.11 g (0.15 mmol) of **5** and hexane (3.0 mL) and another with 0.67 g (0.93 mmol), also in hexane (3.0 mL). Both tubes were evacuated and the solutions degassed and then heated at 110 °C. The extent of isomerization was monitored by ³¹P{¹H} NMR, as before. From the relative heights of the ³¹P{¹H} NMR resonance of **5** to those of **5i**, it appeared that the dilute solution of **5** isomerized faster than the concentrated one. In a third study solid **5** was heated under vacuum at 115 °C for 40 h. A ³¹P{¹H} NMR spectrum of the resulting solid in hexane showed it consisted almost entirely of **5i** with traces of **5**. The melting point reported for **5** (Table I and ref 6) is almost certainly due to that of **5i**.

The mass spectrum of **5i** obtained by using chemical ionization (CH₅⁺) exhibited only a very weak set of peaks due to the parent ion; the most intense peaks in the spectrum were due to (P – CH₃)⁺.

{Ru[P(OMe)₃]₅(CH₃)}I. A solution of **5** (0.71 g, 0.98 mmol) and CH₃I (1.0 mL, 16 mmol) was stirred for 24 h (a white precipitate began to form after ca 5 min). After the 24-h period, the hexane and excess CH₃I were removed on the vacuum line. The remaining very pale yellow solid was washed with hexane (2 × 5 mL) and dried on the vacuum line. The product {Ru[P-(OMe)₃]₅(CH₃)}I (0.81 g, 96%), obtained as white powder, was analytically pure.

The rate of reaction appeared to depend on the concentration of CH₃I. Thus the reaction of a dilute solution of **5** with a large excess of CH₃I was complete in approximately 15 min, as ascertained by ³¹P{¹H} NMR spectroscopy.

When **5i** was used in place of **5**, in similar experiments to the two described above, {Ru[P(OMe)₃]₅(CH₃)}I (6) was produced in almost identical yield. The product was identified by melting point and ³¹P{¹H} NMR spectrum.

A solid sample of **6** was heated at 70 °C under active vacuum for 24 h. A ³¹P{¹H} NMR spectrum of the solid in CH₂Cl₂ indicated no change from that of the starting material. The solvent was removed, and the solid was heated at 100 °C under vacuum for a further 24 h. A ³¹P{¹H} NMR spectrum of the sample (in CH₂Cl₂) indicated that it was mainly unchanged. A weak set of signals were present, but these were not due to either **5** or **5i**.

(H)R̄u[(C₆H₄O)P(OPh)₂][P(OMe)₃]₃. A solution of Ru-(CO)₂[P(OMe)₃]₃ (0.50 g, 0.94 mmol) and P(OPh)₃ (0.71 g, 2.2 mmol) in hexane (20 mL) was irradiated with UV light for 48 h, in the usual manner. During the irradiation a white solid slowly formed. After the 48-h period, an infrared spectrum of the solution indicated complete reaction of **3**. The solution and white solid were transferred to a Schlenk flask. The hexane was removed under vacuum and the remaining white solid recrystallized from hexane/CH₂Cl₂ (20:1) to give (H)R̄u[(C₆H₄O)P(OPh)₂][P-(OMe)₃]₃ as a colorless, microcrystalline solid. Although not measured, the yield appeared excellent. The compound can be handled for several days in air without apparent decomposition, although it does eventually yellow in air.

Results and Discussion

The Series Ru(CO)₅₋ₙ[P(OMe)₃]ₙ (n = 1–5). In this study the five members of the series, Ru(CO)₅₋ₙ[P-(OMe)₃]ₙ, have been prepared and characterized (Table I). Similar complete series of substituted metal carbonyl derivatives are not common. The iron analogues with n = 1, 2,¹² 3,⁵,¹² and 5⁴,⁵ are well characterized. However, the case for Fe(CO)[P(OMe)₃]₄⁵ is not strong especially in view of the properties found for Ru(CO)[P(OMe)₃]₄ (vide infra). The present series is reminiscent of the M(CO)₅₋ₙ(PF₃)ₙ (M = Fe,¹³ Ru¹⁴) groups of molecules. For the PF₃ compounds, the various possible axial–equatorial isomers of each molecule were detected in solution which was not observed for the trimethyl phosphite derivatives.

The use of UV irradiation, as in the preparation of Ru[P(OMe)₃]₅ from Ru₃(CO)₁₂, has been employed previously in the synthesis of highly substituted metal carbonyl derivatives. It has, for example, been used in the preparation of Fe(PF₃)₅¹³ and of penta- and hexasubstituted derivatives of group 6A hexacarbonyls including Mo[P(OMe)₃]₆.⁸

The synthesis and structure of the first member of the series, Ru(CO)₄[P(OMe)₃] (1), have been recently reported from these laboratories.⁷ The crystal structure of **1** revealed a trigonal-bipyramidal geometry about the ruthenium atom, with the phosphite ligand in the axial position. The phosphite ligand did not have the expected threefold

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Table I. Analytical and Spectroscopic Data

compd[a]	mp, °C	%C calcd	%C found	%H calcd	%H found	%P calcd	%P found	mol wt calcd	mol wt found[b]	$\nu(CO)$,[c] cm^{-1}	^{1}H NMR,[d] ppm	^{31}P{^{1}H} NMR, ppm
$Ru(CO)_3[P(OMe)_3]_2$ (**2**)	54–55	24.95	25.10	4.19	4.14			434	434	2005 (vw), 1933 (s), 1923 (s)	3.72 (17), 3.66 (20), 3.60 (16)[e]	−170.1[c]
$Ru(CO)_2[P(OMe)_3]_3$ (**3**)	90–91	24.96	25.21	5.14	5.30	17.55	17.10	530	530	1948 (m), 1894 (s)	3.61 (5), 3.57 (3), 3.53 (3), 3.49 (5)[f]	−171.9[c]
$Ru(CO)[P(OMe)_3]_4$ (**4**)	175–179	24.97	24.79	5.80	5.79	19.81	19.57	626	626	1893 (m)	3.56 (16), 3.49 (mt, 15), 3.45 (17)[f]	−169.7[c]
$Ru[P(OMe)_3]_5$ (**5**)	190–191	25.01	25.06	6.29	6.66	21.49	22.41	722	722		3.58 (6), 3.50 (mt, 9), 3.41 (5)[e]	−166.5[c]
$Ru[P(OMe)_3]_4(CH_3)[P(O)(OMe)_2]$ (**5i**)	190–191	25.01	24.98	6.29	6.24	21.49	21.15	722	722[g]		−0.02, 3.65 (6), 3.63 (2), 3.56 (3), 3.49 (3)[e,h]	i
{$Ru[P(OMe)_3]_5(CH_3)$}I (**6**)	185–187	22.26	22.05	5.60	5.48	17.94	18.36				−0.13 (mt), 3.65 (mt)[e]	−137.2[k]
$(H)Ru[(C_6H_4O)P(OPh)_2][P(OMe)_3]_3$	134–135	41.39	41.20	5.40	5.39	15.81	15.64	784	784		3.39 (mt), 7.08 (mt), −9.22 (mt)[e]	−181.0 (w, mt), −164.5 (s, mt), −154.0 (m, mt)[e]

[a] For Ru(CO)₄[P(OMe)₃] see ref 7; ^{31}P{^{1}H} NMR for 1 (hexane solution): 161.9 ppm. [b] By mass spectroscopy (calcd for ^{102}Ru). [c] Hexane solution. [d] Relative intensities in parentheses; mt = multiplet, most intense peak quoted. [e] CDCl₃ solution. [f] Acetone-d_6 solution. [g] Parent ion very weak. [h] ^{31}P decoupled. [i] See Figure 1. [j] % I: calcd, 14.70; found, 15.20. [k] CH₂Cl₂ solution.

symmetry: one methyl group pointed directly up from the plane of the oxygen atoms, the other two down at an angle. This asymmetry probably persists, on the infrared time scale, in solution. This gives rise to the splitting of the lowest energy carbonyl stretching vibration observed in the solution infrared spectrum of the compound.[7] A similar argument can be applied to account for the two CO stretching absorptions observed in the infrared spectrum of the bissubstituted derivative, $Ru(CO)_3[P(OMe)_3]_2$ (**2**). Trigonal-bipyramidal molecules of formula $M(CO)_3L_2$ with the L groups in the axial positions (D_{3h} symmetry) normally exhibit only one such CO absorption.[15] A similar result (and conclusion) has been obtained for $Fe(CO)_3[P(OMe)_3]_2$, the crystal structure of which revealed the same asymmetry for the phosphite ligands.[16]

Treatment of $Ru_3(CO)_{12}$ in hexane with a large excess of $P(OMe)_3$ gave **1** and **2** (in a ratio of ca. 1.7:1). There were traces of other, more deeply colored, species. One of these was identified as $Ru_3(CO)_9[P(OMe)_3]_3$. It is possible that the other, still more minor, components were $Ru_3(CO)_{12-n}[P(OMe)_3]_n$ ($n = 1, 2$). Poë and Twigg[17] have carried out a detailed investigation of the reaction of $Ru_3(CO)_{12}$ and PBu_3 which gives analogous products to the $P(OMe)_3$ case. In order to account for the 2:1 ratio of the mononuclear products, it was proposed that the monosubstituted cluster $Ru_3(CO)_{11}(PBu_3)$ undergoes fission, since (as has also been found in the present case) the monosubstituted compound, $Ru(CO)_4L$, does not readily give $Ru(CO)_3L_2$ under the reaction conditions. The formation of the trisubstituted cluster, $Ru_3(CO)_9[PBu_3]_3$, was believed to arise from the combination of mononuclear intermediates. Many compounds of the type $Ru_3(CO)_9L_3$, including $Ru_3(CO)_9[P(OMe)_3]_3$, have been described in the literature.[11] There was no report of mononuclear intermediates involved in the formation of these compounds, although the conditions used in their preparation were more vigorous than those used in this study.

The monomeric products **1** and **2** may be separated by fractional sublimation at 0 °C or by column chromatography. Both are somewhat light sensitive, colorless solids that can be handled for short periods in air without apparent decomposition. The monosubstituted compound **1** appeared somewhat thermally unstable, slowly decomposing at room temperature, even under nitrogen in the dark. The preparation of **2** from $Ru(CO)_3(\eta^4\text{-}C_8H_8)$ has appeared in the literature;[18] the physical properties reported are in good agreement with those found here (Table I).

The reaction in an evacuated sealed tube of $Ru_3(CO)_{12}$ and excess $(P(OMe)_3$ in hexane at 100 °C gives, with periodic removal of carbon monoxide, almost exclusively $Ru(CO)_2[P(OMe)_3]_3$ (**3**) after 72 h. (Prolonged reaction at 135 °C did give some of the tetrasubstituted derivative.) The compound, **3**, was isolated as very pale yellow, somewhat air-sensitive, crystals.

The crystal structures of **1**[7] and $Fe(CO)_3[P(OMe)_3]_2$[16] reveal the transition metal to have trigonal-bipyramidal coordination. The same geometry was indicated for $Ru[P(OMe)_3]_5$ by the A_2B_3 pattern observed in the low-temperature ^{31}P{^{1}H} NMR spectrum of the compound.[6] It is tempting to assume that $Ru(CO)_2[P(OMe)_3]_3$ and $Ru(CO)[P(OMe)_3]_4$ (**4**) also have a trigonal-bipyramidal arrangement of ligands about the ruthenium atom. However,

(15) Cotton, F. A.; Parish, R. V. *J. Chem. Soc.* **1960**, 1440. Adams, D. M. "Metal-Ligand and Related Vibrations"; St. Martin's Press: New York, 1968; p 104.

(16) Ginderow, D. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2798.

(17) Poë, A.; Twigg, M. V. *Inorg. Chem.* **1974**, *13*, 2982.

(18) Burt, R.; Cooke, M.; Green, M. *J. Chem. Soc. A* **1970**, 2975.

the structure of these derivatives cannot be deduced from the available spectroscopic evidence. It is conceivable that the configuration in **3** and **4** is square pyramidal or intermediate between square pyramidal and trigonal bipyramidal. Such an intermediate configuration has been observed in $Ru(CO)_4(SbPh_3)$ (with the $SbPh_3$ in an equatorial position).[19] Also, structural studies on compounds of the type $FeL_3(diene)$,[20] and the structure of $Fe[P(OMe)_3]_3(\eta^3-C_8H_{13})$,[21] have found a coordination about the iron atom more nearly described as square pyramidal.

The $^{31}P\{^1H\}$ NMR spectrum of **3** is a singlet even at -120 °C (CCl_2FH solution). Barring accidental degeneracy of signals, this probably indicates the compound is nonrigid since a symmetric structure would not be expected to give two carbonyl stretching absorptions in the infrared spectrum.

Although $Ru(CO)[P(OMe)_3]_4$ (**4**) was observed in the synthesis of $Ru[P(OMe)_3]$ (**5**), the method of preparation of **4** preferred in this study was by the irradiation of **5** in hexane under an atmosphere of carbon monoxide. Small amounts of **3** were removed from the product by sublimation and recrystallization which avoided the need for column chromatography. As isolated, **4** is a waxy, air-sensitive solid. The wax-like nature of **4** and **5** is hardly surprising since the periphery of these molecules must consist mainly of methyl groups.

The value of $\nu(CO)$ for **4** is almost coincident with that of the lowest energy CO stretching frequency of **3** (Table I). This is in contrast to the derivatives **1**, **2**, and **3** where there is a shift to lower energies of the CO stretching vibrations with increasing phosphite substitution.

The suggestion[5] that the product with a CO band at 1990 cm⁻¹ (formed from the reaction of $Fe[P(OMe)_3]_5$ and CO) is $Fe(CO)[P(OMe)_3]_4$ is probably not correct. In the two series of molecules $M(CO)_{5-n}[P(OMe)_3]_n$ (M = Fe, Ru) the CO stretching frequencies of the iron derivatives with n = 1–3 are all some 10–20 cm⁻¹ lower than their ruthenium counterparts[22] ($\nu(CO)$ for **4** is 1893 cm⁻¹).

The $^{31}P\{^1H\}$ NMR spectrum of **4** in CCl_2FH was similar to **3** in that it consisted of a single resonance even at -120 °C. The actual ^{31}P chemical shift of **4** and the other members of the series do not vary in a consistent manner (Table I). There is a significant change downfield between the resonance of **2** and that of **1**. There is a small downfield shift on going to **3** from **2**. However, from **3** to **4**, and from **4** to **5**, the shift is upfield. The theory of ^{31}P chemical shifts of transition-metal complexes with phosphorus donor ligands is not well understood,[24] and doubtless there are a number of factors of importance influencing the chemical shifts of the molecules of the present series. It has been proposed that changes in the bond angles (and hence the hybridization) of the phosphorus atom has a major effect on the chemical shift.[24] In the more highly substituted members of the series, **4** and **5**, the angles about the phosphorus atoms could be different to those in the molecules with n = 1 and 2 due to increased steric inter-
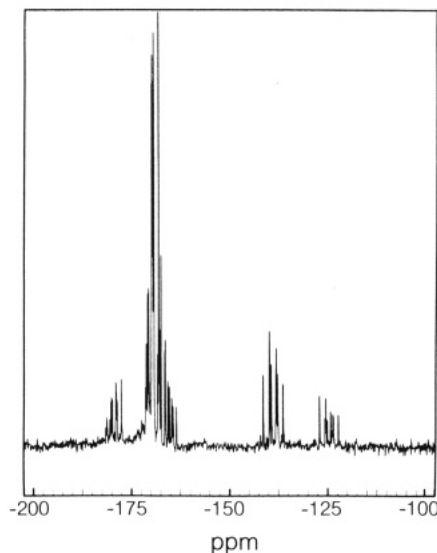

Figure 1. The 40.5-Hz $^{31}P\{^1H\}$ NMR spectrum of $Ru[P(OMe)_3]_4(CH_3)[P(O)(OMe)_2]$ in CH_2Cl_2.

actions in the former compounds.[25] In $\{Ni[P(OMe)_3]_4Br\}^+$[26] the conformations of the phosphite groups were different to that which is found in most other complexes with this ligand.[7]

The last member of the series $Ru[P(OMe)_3]_5$, **5**, was prepared by the UV irradiation of $Ru_3(CO)_{12}$ and excess $P(OMe)_3$ in hexane, with periodic removal of carbon monoxide. The reaction was carried out in Pyrex apparatus as irradiation of $P(OMe)_3$ in quartz vessels caused it to break down into products which were difficult to remove from **5**. Not unexpectedly, there was both infrared and NMR evidence for the other members of the series, with n = 1–4, during the synthesis of **5**. Prolonged irradiation of **5** in hexane caused its conversion to at least two compounds which have not been identified.

Like **4**, **5** is a white, waxy solid. It is very air-sensitive. It is also extremely soluble in hexane, which is not surprising since this fluxional molecule should have virtually no dipole moment and its external surface should contain only methyl groups. English et al.[6] have previously prepared **5** by the sodium amalgam reduction of $Ru[P(OMe)_3]_4Cl_2$ in the presence of excess phosphite in tetrahydrofuran solution.[28] They also reported that the singlet, observed in the $^{31}P\{^1H\}$ NMR spectrum of a solution of **5** at ambient temperature, collapses to an A_2B_3 pattern at low temperatures (-125 °C).[6] We have confirmed this observation.

Preliminary attempts to extend the present method of synthesis to $M[P(OMe)_3]_5$ (M = Fe, Os) have been unsuccessful. For $Fe(CO)_5$, a brown oil was produced in the reaction which did not show any carbonyl absorptions in the infrared spectrum. It also did not exhibit any sharp

(19) Forbes, E. J.; Jones, D. L.; Paxton, K.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1979**, 879.

(20) Mills, O. S.; Robinson, G. *Acta Crystallogr.* **1963**, *16*, 758. Cotton, F. A.; Day, V. W.; Frenz, B. A.; Hardcastle, K. I.; Troup, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 4522.

(21) Harlow, R. L.; McKinney, R. J.; Ittel, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 7496.

(22) Ref 23 lists $\nu(CO)$ of $Fe(CO)[P(OMe)_3]_4$ as 1864 cm⁻¹. (A reviewer has indicated this value was obtained by monitoring the reaction of $Fe[P(OMe)_3]_5$ and $Fe(CO)_5$ by infrared spectroscopy.)

(23) Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 3432.

(24) Pregosin, P. S.; Kunz, R. W. "³¹P and ¹³C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: New York, 1979; p 47 and references therein.

(25) It might be argued that substitution in the equatorial positions causes the upfield shift in the ^{31}P resonances of the $P(OMe)_3$ groups in **4** and **5**. However, in the $^{31}P\{^1H\}$ NMR spectrum of **5**, in the region of slow exchange, the resonance due to the equatorial $P(OMe)_3$ substituents is some 24-ppm downfield from those in the axial position (a situation which is reversed in the iron compound).[6]

(26) The geometry about the central atom in this cation is essentially trigonal bipyramidal with Br in an equatorial position.[26]

(27) Milbrath, D. S.; Springer, J. P.; Clardy, J. C.; Verkade, J. C. *Inorg. Chem.* **1975**, *14*, 2665.

(28) The iron analogue, and the incompletely characterized osmium compound, were prepared in a similar manner. Metal atom vapor techniques have also been used to prepare $Fe[P(OMe)_3]_5$ (see footnote 1, ref 31).

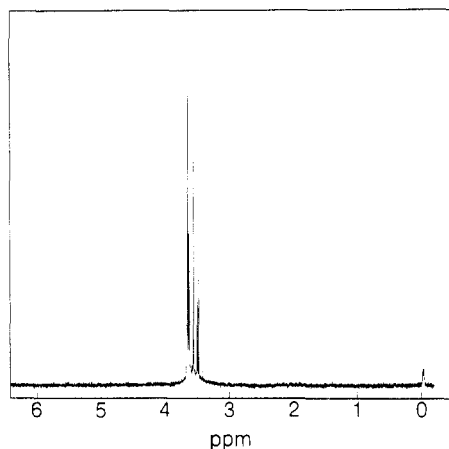(29) Tolman, C. A.; English, A. D.; Ittel, S. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 2374.

Figure 2. The 400-MHz ^{1}H NMR spectrum of Ru[P(OMe)$_3$]$_4$-(CH$_3$)[P(O)(OMe)$_2$] in CDCl$_3$. The spectrum is partially phosphorus decoupled; the high field doublet of the methoxy resonances can also be collapsed to a singlet (at 3.49 ppm) by phosphorus decoupling.

NMR signals (CH$_2$Cl$_2$ solution) which suggested the product was paramagnetic or at least contained paramagnetic impurities. For Os$_3$(CO)$_{12}$ an insoluble orange adduct formed which prevented further reaction. (Experiments in an attempt to circumvent the latter problem are comtemplated.)

Methyl Migration in Ru[P(OMe)$_3$]$_5$. When a solution of 5 in hexane was heated to 120 °C in an evacuated sealed tube for 24 h it was converted into a less soluble, more air-stable, white solid (5i). The new compound also analyzed as Ru[P(OMe)$_3$]$_5$ (Table I). However, unlike 5 which exhibits only a singlet, 5i gave a complex multiplet in the ^{31}P{^{1}H} NMR spectrum (Figure 1). Furthermore, the ^{1}H NMR spectrum of 5i showed a broad resonance at δ –0.02 which sharpened on partial ^{31}P decoupling (Figure 2). Previously, it has been observed that the protons of Ru–CH$_3$ linkages occur in this region of the ^{1}H NMR spectrum.[30,31] On this evidence and the reaction (reported below) of both 5 and 5i with MeI to give {Ru[P(OMe)$_3$]$_5$-(CH$_3$)}I, the structure of 5i is formulated as Ru[P-(OMe)$_3$]$_4$(CH$_3$)[P(O)(OMe)$_2$]. The isomerized product thus involves migration of a methyl group from a phosphite ligand to the metal.

A band in the infrared spectrum of a hexane solution of 5i at 1135 cm^{-1}, which is not present in 5, may be assigned to ν(P=O).[31] The complex ^{31}P{^{1}H} NMR spectrum is consistent with an A$_2$BCD pattern expected for 5i.

The methoxy resonances in the ^{1}H{^{31}P} NMR spectrum of 5i (Figure 2) are also consistent with the formulation: δ 3.49, 3.56, 3.63, and 3.65 in the ratio ca. 3:3:2:6. In the ^{31}P coupled spectrum each resonance is split into a doublet ($J_{P-H} = 10$ Hz) except that at 3.65 ppm (assigned to the axial P(OMe)$_3$ ligands) which is split into a triplet (apparent $J_{P-H} = 5$ Hz) due to strong phosphorus–phosphorus coupling.[32] (Strong phosphorus–phosphorus coupling is also observed in the ^{1}H NMR spectrum of 2.) It is interesting that the other pair of *trans* phosphorus atoms (one of which is part of the P(O)(OMe)$_2$ group) do not show this strong ^{31}P–^{31}P coupling. It may be that the strong interaction arises mainly because of the π bonding

of the phosphorus atoms with common d orbitals on the ruthenium. In the case of the phosphonate ligand Ru–P π bonding may be considerably reduced because of dπ–pπ bonding of the phosphorus to the unique oxygen atom. the Cr–P (phosphonate) distance (2.360 Å), found in (C$_5$H$_5$)-Cr(CO)$_2$[P(OMe)$_3$][P(O)(OMe)$_2$],[33] is greater than the Cr–P (phosphite) distance (2.267 Å), which is consistent with less double-bond character in the former linkage.

There are several examples in the literature of the interaction of a phosphite (P(OR)$_3$) with a transition-metal complex to give products with a M–R or M–P(O)(OR)$_2$ group, or both.[31,33-37] This appears to be the first case where the product has both linkages present in the same molecule although recently the migration of a phenyl group from phosphorus to iron has been reported.[38] In the reaction of (C$_5$H$_5$)M(CO)$_3$(AsMe$_2$) (M = Mo, W) with P(OMe)$_3$, the methyl group transferred to the arsenic atom to give (C$_5$H$_5$)Mo(CO)$_2$[P(O)(OMe)$_2$](AsMe$_3$).[35]

The mechanism by which the alkyl group is lost from the phosphite is uncertain, if indeed it proceeds by the same route in all cases. Thus Alper and co-workers favored an intramolecular mechanism for the reaction of P(OR)$_3$ with (C$_5$H$_5$)$_2$Mo$_2$(CO)$_4$(R'$_2$CS) to give (C$_5$H$_5$)Mo(CO)$_2$-(R'$_2$CS)R.[36] Howell and Rowan preferred the involvement of radical intermediates in the formation of (C$_5$H$_5$)Ru-(CO)$_2$R and (C$_5$H$_5$)Ru(CO)$_2$[P(O)(OR)$_2$] from [(C$_5$H$_5$)Ru-(CO)$_2$]$_2$ and the appropriate phosphite.[31] This pathway was also indicated in the reaction of [(C$_5$H$_5$)Cr(CO)$_2$P-(OMe)$_3$]$_2$ with P(OMe)$_3$, to give similar products.[33] However, in the analogous reaction of the molybdenum complex, [(C$_5$H$_5$)Mo(CO)$_3$]$_2$, with phosphites, Haines and Nolte found clear evidence for ionic intermediates.[37]

In some preliminary studies on the mechanism of the present rearrangement, it has been found that the isomerization is markedly suppressed by free trimethyl phosphite and that dilute solutions of 5 isomerize faster than concentrated solutions. This suggests that the rearrangement of 5 (which formally is an intramolecular oxidative addition) proceeds via the 16-electron species Ru[P(OMe)$_3$]$_4$ arising from the equilibrium

$$\text{Ru[P(OMe)}_3]_5 \rightleftharpoons \text{Ru[P(OMe)}_3]_4 + \text{P(OMe)}_3$$
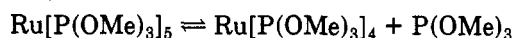
(We have observed that 5 undergoes replacement of P-(OMe)$_3$, by P(OEt)$_3$, at temperatures above 80 °C.) Similar behavior has been observed in the oxidative addition of triphenylphosphine to nickel in Ni(PEt$_3$)$_3$(PPh$_3$).[39]

The present rearrangement also has similarities to the isomerization of P(OMe)$_3$ to MeP(O)(OMe)$_2$. This occurs at 200 °C and is thought to involve the ionic intermediates [MeP(OMe)$_3$]$^+$ and [P(O)(OMe)$_2$]$^-$.[40] This reaction is catalyzed by CH$_3$I in the well-known Michaelis–Arbuzov reaction.[41] However, treatment of a solution of either 5 or 5i with excess methyl iodide gives, within a short period (depending on the concentration of CH$_3$I), an almost quantitative yield of {Ru[P(OMe)$_3$]$_5$CH$_3$}$^+$I$^-$ (6). The re-

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(37) Haines, R. J.; Nolte, C. R. *J. Organomet. Chem.* **1970,** *24,* 725.

(38) Vierling, P.; Riess, J. G.; Grand, A. *J. Am. Chem. Soc.* **1981,** *103,* 2466.

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action of **5** or **5i** with CD$_3$I was as expected. With **5**, the product did not show the ^{1}H NMR resonances centered at −0.13 ppm which are present in **6** and assigned to the methyl protons of the Ru–CH$_3$ linkage. In the ^{1}H NMR spectrum of the derivative obtained by the combination of CD$_3$I and **5i** these resonances were observed. These results are, therefore, in contrast to the Michaelis–Arbuzov reaction where the ionic intermediates, analogous to **6**, usually have only a fleeting existence in the conversion of the trialkyl phosphonate to the alkylphosphonate diester.[42] The results may also be compared with those of Neukomm and Werner[43] who found that treatment of (C$_5$H$_5$)Rh[P-(OMe)$_3$]$_2$ with CH$_3$I, at −30 °C in acetone gave {(C$_5$H$_5$)-Rh(CH$_3$)[P(OMe)$_3$]$_2$}I. This, on warming to 50 °C, eliminated CH$_3$I to yield the phosphonate complex, (C$_5$H$_5$)-Rh(CH$_3$)[P(OMe)$_3$][P(O)(OMe)$_2$].[44]

The ^{31}P{^{1}H} NMR spectrum (at 40.5 MHz) of **6** in CH$_2$Cl$_2$ solution consists of a singlet at room temperature. The spectrum of the solution at −90 °C shows a number of satellites, which are not symmetric, about the main peak. This probably indicates that the chemical shifts of the two types of phosphorus nuclei in the rigid, octahedral {Ru-[P(OMe)$_3$]$_5$(CH$_3$)}$^+$ cation are accidentally degenerate at room temperature. However, different temperature dependencies of the two signals cause them to become inequivalent at −90 °C, such that an AB$_4$ pattern is observed. The low-temperature spectrum can be successfully simulated by assuming an AB$_4$ spin system. Marked temperature dependencies of the ^{31}P NMR signals of **5**, and its

derivatives have been observed in this and other studies in this laboratory.

Synthesis of (H)$\overline{\text{Ru}[(\text{C}_6\text{H}_4\text{O})}$P(OPh)$_2$][P(OMe)$_3$]$_3$. From the ultraviolet irradiation of **3** in hexane with P-(OPh)$_3$ a white, crystalline solid was isolated which analyzed as Ru[P(OMe)$_3$]$_3$[P(OPh)$_3$] (**7**). This compound exhibited a complex pattern in the ^{31}P{^{1}H} NMR spectrum which suggested the P(OMe)$_3$ ligands are not equivalent. In the ^{1}H NMR spectrum, besides aromatic and methoxy protons, there was a multiplet centered at δ −9.25 indicative of a metal hydride bond. On this evidence, **7** is formulated as the ortho-metalated compound, (H)$\overline{\text{Ru}[(\text{C}_6\text{H}_4\text{O})\text{P}}$-(OPh)$_2$][P(OMe)$_3$]$_3$. Similar behavior has been observed previously in triphenyl phosphite derivatives of ruthenium.[29]

It is apparent from this and other studies[5,46] that oxidative addition at the electron-rich metal center in molecules of this type is a facile process. This and other aspects of the chemistry of Ru[P(OMe)$_3$]$_5$ are under further investigation.

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(44) The phosphonate complex is also an intermediate in the reaction of (C$_5$H$_5$)Rh[P(OMe)$_3$]$_2$ with alkali-metal iodides.[45]

(45) Werner, H.; Feser, R. *Z. Anorg. Allg. Chem.* **1979**, *458*, 301.

(46) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. "Inorganic Compounds with Unusual Properties"; King, R. B., Ed.; American Chemical Society: Washington, DC, 1979; Vol. II, p 67.