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Olefin Complexes of Divalent Ruthenium Formed by Chelating Olefinic Tertiary Phosphines and Arsines

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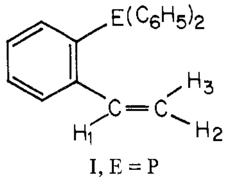
Received July 23, 1973

o-Styryldiphenylphosphine (SP) and *o*-styryldiphenylarsine (SPAS), *o*-CH_2=$CHC_6H_4E(C_6H_5)_2$ (E = P or As), react with hydrated ruthenium(III) halides in alcoholic media to give yellow or brown, monomeric complexes RuX_2(ligand)$_2$ (X = Cl or Br), which are oxidatively and thermally stable. The complex $RuCl_2(SP)_2$ exists in three isomeric forms, of which one can be isolated in an isomerically pure state. Infrared and nmr (^1H and ^{31}P) data are used to assign the stereochemistry of the complexes and to show that both the group V atom and the vinyl group of SP or SPAS are attached to the ruthenium atom. The coordinated vinyl groups of $RuCl_2(SP)_2$ are displaced by CO to give $RuCl_2(CO)_2(SP)_2$, two isomers of which can be isolated; both of these contain monodentate P-bonded SP. Reaction of SP with ruthenium chloride in the presence of CO gives colorless $RuCl_2(CO)_2(SP)$, which reversibly loses CO on heating to give two yellow, isomeric, dimeric complexes $[RuCl_2(CO)(SP)]_2$, which probably contain bridging chlorine atoms. The last three complexes contain bidentate SP as shown by their ir and nmr (^1H and ^{31}P) spectra. Reaction of $[RuCl_2(CO)_3]_2$ with SP in benzene gives initially $RuCl_2(CO)_3(SP)$, which contains monodentate P-bonded SP, but in refluxing 2-methoxyethanol the complex loses CO to give the isomers of $[RuCl_2(CO)(SP)]_2$. The chelate complexes of SP and SPAS are the first monoolefin complexes of ruthenium(II) to be isolated. The conditions under which ruthenium(II)–ethylene complexes might be isolated are briefly discussed.

Introduction

Although stable complexes of divalent ruthenium with chelating diolefins such as 1,5-cyclooctadiene, norbornadiene, cyclooctatetraene, and cycloheptatriene are well known,[1-7] there are no known analogous monoolefin complexes. Blue solutions obtained by the reduction of ruthenium(III) chloride form 1:1 complexes of ruthenium(II) with ethylene, norbornene, maleic acid, fumaric acid, and 5-norbornene-2,3-dicarboxylic anhydride in solution, but these species have not been isolated.[8] There is also evidence for olefin coordination in acrylonitrile complexes of ruthenium(II),[9,10] and a complex $RuCl_2(CO)(C_8H_{12})\{P(C_6H_5)_3\}_2$ which may contain monodentate 4-vinylcyclohexene has been isolated.[11] Tertiary arylphosphines and arsines containing an *o*-vinyl or *o*-allyl group, such as *o*-styryldiphenylphosphine, *o*-CH_2=$CHC_6H_4P(C_6H_5)_2$, and *o*-allylphenyldiphenylphosphine, *o*-CH_2=$CHCH_2C_6H_4P(C_6H_5)_2$, and their dimethylarsino analogs, are known to be powerful chelate ligands which stabilize olefin coordination to a variety of transition elements,[12-18] and we now show that *o*-styryldiphenylphosphine, SP (I; E = P), and *o*-styryldiphenylarsine, SPAS (II; E = As), form stable chelate olefin complexes with divalent ruthenium.



I, E = P
II, E = As

Experimental Section

Starting Materials. All solvents were dried over molecular sieve (BDH 4A or 5A). *o*-Styryldiphenylphosphine and *o*-styryldiphenylarsine were prepared as described previously[12] from the Grignard reagent of *o*-bromostyrene in THF and chlorodiphenylphosphine or chlorodiphenylarsine. Di-*μ*-chloro-bis(chlorotricarbonyl)diruthenium(II), $[RuCl_2(CO)_3]_2$, was prepared by heating hydrated ruthenium trichloride with formic acid and concentrated hydrochloric acid for 24 hr. Under these conditions, the product was $[RuCl_2(CO)_3]_2$, as stated by Cleare and Griffith,[19] not polymeric $[RuCl_2(CO)_2]_n$, as reported by Colton and Farthing.[20] The ir spectrum in the ν(CO) region agreed with that given by Bruce and Stone[21] and by Cleare and Griffith,[19] and the mass spectrum showed the parent dimeric ion $[Ru_2Cl_4(CO)_6]^+$, together with fragment ions $[Ru_2Cl_4(CO)_n]^+$ (n = 0–5), $[Ru_2Cl_3(CO)_6]^+$, $[Ru_2Cl_n]^+$ (n = 0–4), $[RuCl_2]^+$, and $[RuCl]^+$. Addition of 1 equiv of cesium chloride to a solution of $[RuCl_2(CO)_3]_2$ in concentrated hydrochloric acid gave $Cs[RuCl_3(CO)_3]$, but with an excess of cesium chloride this reacted further to give $Cs_2[RuCl_4(CO)_2]$.[19]

Measurements. Infrared spectra were recorded on Perkin-Elmer 457 or 225 spectrophotometers calibrated with polystyrene. Solid state spectra were taken as Nujol mulls on either KBr or CsI windows; solution spectra were measured in 1-mm path length cells having CaF_2 windows. Proton nmr spectra were recorded on a Varian HA-100 instrument with TMS as internal reference. Phosphorus nmr spectra were recorded on a Jeol C60-HL spectrometer modified for proton decoupling. Mass spectra were measured on an AEI MS-9 instrument at 70 eV (Mr. K. Goggin). Analyses and osmometric molecular weight determinations (Mechrolab Model 301A) were carried out by the

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Microanalytical Laboratories of the Research School of Chemistry and the John Curtin School of Medical Research, Australian National University (Miss Brenda Stevenson and Dr. Joyce Fildes and their associates). Analytical data are in Table I.

Preparations. Dichlorobis(*o*-styryldiphenylphosphine)ruthenium(II), $RuCl_2(SP)_2$, 1a. *o*-Styryldiphenylphosphine (0.8 g, 3.5 mol per g-atom of Ru) and hydrated ruthenium trichloride (containing ~40% Ru) (0.2 g) in 2-methoxyethanol (40 ml) were stirred and heated under reflux for 1.5 hr in a nitrogen atmosphere. The initially deep red solution turned green and at the reflux temperature a yellow precipitate formed together with a black sludge (presumably ruthenium metal). After cooling to room temperature, the supernatant solution was decanted and the solid was washed with methanol. The solid was dissolved in boiling dichloromethane (20 ml), the solution was filtered, and methanol (50 ml) was added to the filtrate to give a deep yellow crystalline precipitate. This was washed by decantation with methanol and dried first in a stream of nitrogen and finally at 60° (10^{-3} mm): yield of 1a, 0.43 g (73%); mass spectrum, *m/e* 748 [parent ion, $^{102}Ru^{35}Cl_2(SP)_2$].

$RuCl_2(SP)_2$, Isomeric Mixture of 1b and 1c. This was prepared as described above using ethanol in place of 2-methoxyethanol and a reaction time of 30–40 min: yield of yellow product, 0.38 g (65%). The ratio of **1b** to **1c** determined from the proton-noise-decoupled ^{31}P nmr spectrum (Table II) was about 3 to 2.

The following three complexes were also prepared as described above.

Dibromobis(*o*-styryldiphenylphosphine)ruthenium(II), $RuBr_2(SP)_2$, 2: orange crystals from hydrated ruthenium tribromide (0.2 g), *o*-styryldiphenylphosphine (0.5 g), and 2-methoxyethanol (40 ml), with a reflux time of 1.5 hr; yield, 0.15 g (32%); mass spectrum, *m/e* 838 [parent ion, $^{102}RuBr_2(SP)_2$]. No product was obtained using ethanol as solvent.

Dichlorobis(*o*-styryldiphenylarsine)ruthenium(II), $RuCl_2(SPAS)_2$, 3: yellow-brown solid from hydrated ruthenium trichloride (0.2 g), *o*-styryldiphenylarsine (0.8 g), and ethanol (25 ml) with a reflux time of 40 min; yield,0.064 g (10%); mass spectrum, *m/e* 836 [parent ion, $^{102}Ru^{35}Cl_2(SPAS)_2$]. No product was obtained using 2-methoxyethanol.

Dibromobis(*o*-styryldiphenylarsine)ruthenium(II), $RuBr_2(SPAS)_2$, 4: orange-brown solid from hydrated ruthenium tribromide (0.2 g), *o*-styryldiphenylarsine (0.55 g), and 2-methoxyethanol (40 ml) heated under reflux for 1 hr; yield, 0.3 g (59%); mass spectrum, *m/e* 926 [parent ion, $^{102}RuBr_2(SPAS)_2$].

Dichlorodicarbonylbis(*o*-styryldiphenylphosphine)ruthenium(II), $RuCl_2(CO)_2(SP)_2$, 5a and 5b. Carbon monoxide was passed into a suspension of either **1a** or the mixture of **1b** and **1c** (0.4 g) in refluxing 2-methoxyethanol (40 ml) until the solution became colorless (~1 hr). A white precipitate formed when the solution cooled to room temperature. After the supernatant liquid had been decanted, the solid was washed with methanol and dried first in a stream of nitrogen then *in vacuo* to give pure **5a**. The yield was ~20% starting from **1a** and ~50% starting from the mixture of **1b** and **1c**. The supernatant liquid was evaporated to dryness under reduced pressure, and the residue was recrystallized from dichloromethane–*n*-hexane to give colorless crystals of **5b**. This was also obtained by recrystallizing **5a** from dichloromethane–methanol. The yield of combined products was essentially quantitative: mass spectrum, *m/e* 804 [parent ion (weak), $^{102}Ru^{35}Cl_2(CO)_2(SP)_2$].

Dichlorodicarbonyl(*o*-styryldiphenylphosphine)ruthenium(II), $RuCl_2(CO)_2(SP)$, 6. A slow stream of carbon monoxide was passed into a solution of hydrated ruthenium trichloride (0.3 g) and *o*-styryldiphenylphosphine (0.69 g, 2 mol per g-atom of Ru) which was heated under reflux in 2-methoxyethanol (40 ml) for 1 hr. After cooling to room temperature, the solution was evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane (20 ml), the solution was filtered, and colorless crystals of **6** (a 1:1 solvate with CH_2Cl_2) were obtained by cautious addition of *n*-hexane: yield, 0.6 g (84%). The dichloromethane was removed by heating to 75° (10^{-3} mm) for 1 hr. The mass spectrum showed a parent ion at *m/e* 516 due to $[^{102}Ru^{35}Cl_2(CO)_2(SP)]^+$ in addition to peaks associated with the dimeric decomposition product $[RuCl_2(CO)(SP)]_2$, **7** (see below).

Di-μ-chloro-bis[chlorocarbonyl(*o*-styryldiphenylphosphine)]diruthenium(II), $[RuCl_2(CO)(SP)]_2$, 7a and 7b. Complex **6** (0.4 g) in 2-methoxyethanol (40 ml) was heated under reflux in a nitrogen atmosphere for 1 hr. Solvent was removed *in vacuo* and the residue was treated with dichloromethane (20 ml) to give a yellow solid and a deep yellow solution, which was decanted off and retained. The solid was dissolved in chloroform (10 ml), and to the filtered solution was added *n*-hexane to give a yellow, microcrystalline precipitate.

Table I. Analytical Data, Melting Points, and Selected Infrared Bands[a]

Complex	% C		% H		% X		% P (As)		Mp, °C	ν(CO), cm^{-1} [b]	ν(RuCl), cm^{-1} [b]	Vinyl deformation modes, cm^{-1} [b]
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found				
$RuCl_2(SP)_2$ (1a)[c,d]	64.7	64.1	4.6	4.6	9.5	10.1	8.3	7.7	>220 dec		289 s, 265 s	875 w
$RuCl_2(SP)_2$ (1b and 1c)[e]	64.7	62.7	4.6	4.9	9.5	11.4	8.3	7.8	>200 dec		317 s	875 w
$RuBr_2(SP)_2\cdot CH_2Cl_2$ (2)	53.4	53.7	3.9	3.8	34.7[f]	33.5[f]	6.7	6.4	>230 dec			875 w
$RuCl_2(SPAS)_2\cdot CH_2Cl_2$ (3)	53.4	54.6	3.9	4.3	15.4	15.1	16.3	16.4	>220 dec			875 w
$RuBr_2(SPAS)_2\cdot CH_2Cl_2$ (4)	48.7	49.3	3.6	4.2	31.6[f]	31.6[f]	14.8	15.0	>220 dec			875 w
$RuCl_2(CO)_2(SP)_2$ (5a)	62.7	62.7	4.3	4.7	8.8	8.8	7.7	7.2	Nm	2070 s, 2000 s	315 ms, 284 ms	990 m, 930 s[g]
$RuCl_2(CO)_2(SP)_2\cdot CH_2Cl_2$ (5b)	58.1	58.3	4.1	4.1	15.9	15.7	7.0	6.7	Nm	2050 s, 1980 s	316 ms, 290 ms	985 m, 915 s
$RuCl_2(CO)_2(SP)$ (6)	51.2	50.7	3.3	3.3	13.7	14.4	6.0	6.0	>200 dec	2085 s, 2035 s	311 ms, 280 ms	875 w
$[RuCl_2(CO)(SP)]_2$ (7a)[h,i]	51.7	49.2	3.5	3.5	14.5	18.5	6.3	5.7	Nm	1980 s	316 ms	875 w
$[RuCl_2(CO)(SP)]_2$ (7b)	51.7	50.6	3.5	3.9	14.5	15.9	6.3	6.3	Nm	2020 s	305 w	875 w
$RuCl_2(CO)_3(SP)$ (8)	50.8	50.6	3.2	3.5	13.0	13.6	5.7	5.7	Nm	2130 s, 2062 s, 1994 s[j]	308 ms, 283 ms	985 m, 922 m

[a] Abbreviations: X = Cl or Br; s, strong; ms, medium strong; w, weak; nm, not measured. [b] Measured in Nujol mulls. [c] C, Cl, and P analyses are consistent with the presence of ~0.1 mol of CH_2Cl_2 per mol of complex, confirmed by ^1H nmr in $CDCl_3$. [d] Molecular weight in $CHCl_3$ at 37°: calcd, 748; found, 774. [e] C, Cl, and P analyses are consistent with the presence of ~0.3 mol of CH_2Cl_2 per mol of complex, confirmed by ^1H nmr in $CDCl_3$. [f] Total halogen (Cl + Br), calcd as Br. [g] Values for SP: 990 m, 927 s cm^{-1}. [h] C, Cl, and P analyses are consistent with the presence of ~0.5 mol of $CHCl_3$ per mol of dimer, confirmed by ^1H nmr in CD_2Cl_2. [i] Molecular weight in $CHCl_3$ at 25°: calcd, 976; found, 908. [j] 2140 s, 2066 s, 2016 s cm^{-1} (CH_2Cl_2).

Table II. Nmr Data[a]

Complex	Chemical shifts				Coupling constants					
	δ_1[b]	δ_2[b]	δ_3[b]	δ_P[c]	J_{12}[d]	J_{13}[d]	J_{23}[d]	J_{P-H_1}[e]	J_{P-H_2}[e]	J_{P-H_3}[e]
1a	3.30	1.99	2.84	47.2	9.5	12.5	$\leqslant 1$	<1	4.5	<1
1b	5.68	4.68	3.64	41.0	9.5	13.5	$\leqslant 1$	2.0	4.5	3.0
1c	6.34	3.73	4.09	37.4	9.5	14.0	$\leqslant 1$	2.0	5.0	3.5
2	3.30	2.08	3.11	41.7	9.0	12.5	$\leqslant 1$	<1	5.0	<1
3	3.34	2.34	3.09		9.0	12.0	$\leqslant 1$			
5b	6.74	5.04	5.74	Nm	11.0	17.0	1.0	~0	~0	~0
6	*f*	5.20	4.62	Nm	9.0	14.5	1.5	*f*	*g*	*g*
7a	*f*	5.48	3.78	Nm	9.5	13.0	$\leqslant 1.5$	*f*	~0	~0
8	6.73	5.04	5.75	Nm	10.5	17.0	1.0	~0	~0	~0

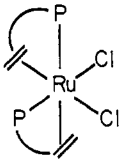
[a] Measured in CD_2Cl_2. Aromatic resonances are complex multiplets in range δ 6.9–8.0. Protons are numbered as in structure I. [b] In ppm downfield from internal TMS, ±0.01 ppm. [c] In ppm downfield from external 85% H_3PO_4, ±0.3 ppm. [d] In Hz, ±0.5. [e] In Hz, ±0.5; average of coupling to two phosphorus atoms for complexes **1a**, **1b**, **1c**, **2**, and **5b**. [f] Obscured by aromatic resonances. [g] Proton resonances are broad and are sharpened slightly by ^{31}P decoupling.

This was centrifuged, washed with *n*-pentane, and dried *in vacuo*. The yield of **7a** was 0.13 g (35%). The dichloromethane solution was treated with benzene (20 ml). On standing, an orange-yellow precipitate formed, which was centrifuged, washed with *n*-pentane, and dried *in vacuo*. The yield of **7b** was 0.21 g (55%). **7b** was also formed from solutions of **7a** in chloroform on heating or on standing overnight and was precipitated by addition of *n*-hexane. Once formed, **7b** is only slightly soluble in chloroform and dichloromethane and insoluble in benzene, acetone, and ethanol: mass spectrum, *m/e* 976 [parent ion, $^{102}Ru_2{}^{35}Cl_4(CO)_2(SP)_2$], with fragments arising from successive, stepwise loss of CO then Cl.

Dichlorotricarbonyl(*o*-styryldiphenylphosphine)ruthenium(II), $RuCl_2(CO)_3(SP)$, 8. A mixture of $[RuCl_2(CO)_3]_2$ (0.25 g) and *o*-styryldiphenylphosphine (0.28 g, 1 mol per g-atom of Ru) in benzene (40 ml) was heated under reflux with stirring in a nitrogen atmosphere for 3 hr. The solution was allowed to cool to room temperature, filtered to remove a small quantity of white, insoluble material, and evaporated to dryness under reduced pressure. The solid product was washed with hot *n*-hexane (2 × 10 ml), dried in a stream of nitrogen, then heated at 45° (10^{-3} mm) to remove traces of solvent; yield, 0.44 g (80%).

Results and Discussion

Reaction of hydrated ruthenium trichloride with SP (>2 mol of ligand per g-atom of Ru) in refluxing ethanol or 2-methoxyethanol gives a complex of formula $RuCl_2(SP)_2$ in yields of 60–70%. In 2-methoxyethanol a deep yellow isomer **1a** is obtained, but in ethanol an inseparable mixture of two other yellow isomers (**1b** and **1c**) is formed, which slowly isomerizes to **1a** on heating in 2-methoxyethanol. The complex $RuBr_2(SP)_2$, **2**, is obtained similarly from ruthenium tribromide in 2-methoxyethanol, and analogous complexes of *o*-styryldiphenylarsine, $RuX_2(SPAS)_2$ (X = Cl, **3**; X = Br, **4**), can also be made. All the complexes are readily soluble in dichloromethane, and they tenaciously retain this solvent on recrystallization from dichloromethane-methanol. Complexes **2**–**4** appear to exist in only one isomeric form. **1a** is monomeric in chloroform, and all the complexes show parent ion peaks in their mass spectra. The three isomers **1a**–**c** can be distinguished by their ^1H and ^{31}P nmr spectra (Table II). The marked upfield shifts of the olefinic protons and the decrease in the magnitudes of the vicinal $^1H-^1H$ coupling constants relative to those in the free ligand indicate that both vinyl groups are coordinated in all three isomers **1a**–**c** and in complexes **2**–**4**. This conclusion is supported by the absence of the infrared olefinic C–H deformation bands at ~990 and ~920 cm^{-1}, which are characteristic of the uncoordinated vinyl group. Also, the ^1H-decoupled ^{31}P nmr spectra for **1a**–**c** and **2** are singlets (Table II), showing that the two phosphorus atoms are equivalent in these compounds, and for this reason, all the resolved $^{31}P-^1H$ couplings to the vinyl protons appear as triplets. The far-ir spectrum of the mixture of **1b** and **1c** shows only one band assignable to ν(RuCl) at 317 cm^{-1}, indicating that the chlorine atoms are mutually trans, whereas **1a** shows two ν(RuCl) bands at 289 and 265 cm^{-1}, indicative of mutually cis chlorine atoms. The following ranges have been quoted[22] for ν(RuCl) in octahedral ruthenium(II) complexes: Cl trans to Cl, 347–299 cm^{-1}, Cl trans to CO, 311–266 cm^{-1}, and Cl trans to PR_3, 262–229 cm^{-1}. Assuming that the trans ligands CO and olefin give rise to similar ν(RuCl) values,[23] one can accommodate the ir data for **1a** on the basis either of structure III (Cl trans to P, Cl trans to olefin) or of structure IV (both Cl atoms trans to olefin). The former is ruled out by the observed equivalence of the vinyl groups and phosphorus atoms in solution, and we therefore prefer IV. The ν(RuCl) values seem too high to be compatible with the alternative structure V, which would also be sterically disfavored by the cis orientation of the bulky triarylphosphino groups.



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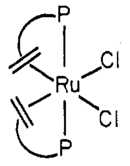
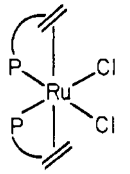


IV



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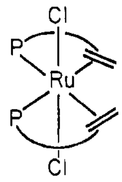

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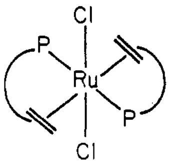

VII

1b and **1c** must have structures VI or VII, but definite assignments cannot be made on the basis of our data. Structure VI resembles V in having *cis*-phosphorus atoms and is presumably disfavored for steric reasons, and VII may be relatively unstable because two strongly π-bonding olefin groups are mutually trans. It is also possible that **1b** and **1c** have identical arrangements of ligand atoms about the ruthenium atom but have different orientations of the two vinyl groups, which, however, must remain equivalent in each isomer. Evidence for this type of isomerism has been obtained

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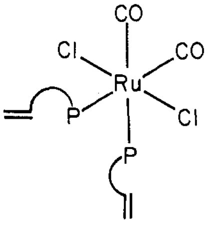
(22) M. S. Lupin and B. L. Shaw, *J. Chem. Soc. A*, 741 (1968).

(23) This assumption is supported by the fact that ν(MCl) in planar rhodium(I) and iridium(I) complexes of general formula MCl(ligand) formed by tridentate olefinic tertiary phosphines such as *trans-o*-$(C_6H_5)_2PC_6H_4CH{=}CHC_6H_4P(C_6H_5)_2$-*o* and *trans-o*-$(C_6H_5)_2PC_6H_4CH{=}CHCH(CH_3)C_6H_4P(C_6H_5)_2$-*o* fall in a similar range (300–320 cm^{-1}) to those observed in the planar carbonyl complexes *trans*-$MCl(CO)\{P(C_6H_5)_3\}_2$: M. A. Bennett, P. W. Clark, and I. B. Tomkins, unpublished work.

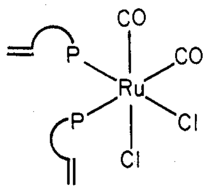
in the octahedral group VI tetracarbonyls of SP and SPAS[24] and in five-coordinate bis(SP) complexes of Rh(I), Ir(I),[25] and Ru(0).[26] The ^{1}H nmr data (Table II) suggest that **2**, **3**, and **4** are structurally similar to **1a**.

The assignments of the vinyl proton resonances in Table II are based on the assumption that $|J_{13}|$(trans) > $|J_{12}|$(cis) in the coordinated vinyl group, as is true for the free vinyl group; the magnitudes of both vicinal (J_{12} and J_{13}) and geminal (J_{23}) coupling constants are approximately equal to the corresponding values for the group VI tetracarbonyl complexes of SP and SPAS.[12,16,24] The chemical shifts of the vinyl protons of **1b** are in the order $\delta_1 > \delta_2 > \delta_3$, which has been observed previously in all the chelate complexes of SP, but **1a** and **1c** are unusual in that the order is $\delta_1 > \delta_3 > \delta_2$, which is also found in SP itself.

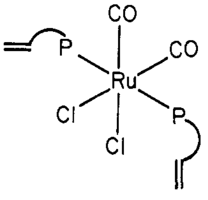
Carbonylation (1 atm) of **1a–c** in refluxing 2-methoxyethanol gives a mixture of two isomeric dicarbonyl complexes $RuCl_2(CO)_2(SP)_2$, one of which, **5a**, precipitates from the reaction mixture. The other isomer, **5b**, remains in solution, and is also formed quantitatively when **5a** is dissolved in dichloromethane. The ^{1}H nmr spectrum of **5b** (Table II) indicates that both vinyl groups are uncoordinated, and both isomers exhibit strong bands in their ir spectra at 990 and 920 cm^{-1} assignable to olefinic C–H deformation modes. Since both isomers also show two strong ν(CO) bands, the carbonyl groups must be mutually cis. The three obvious structural posibilities are VIII (*trans*-chlorine atoms, *cis*-phosphorus atoms), IX (*cis*-chlorine atoms, *cis*-phosphorus atoms), and X (*cis*-chlorine atoms, *trans*-phosphorus atoms).



VIII



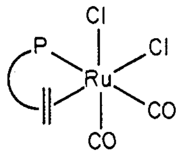
IX



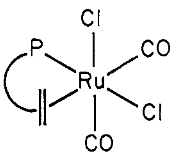
X

Surprisingly, the solid state far-ir spectra of both isomers are very similar and show two strong bands assignable to ν(RuCl) modes (Table I). The positions of these bands for both isomers are consistent with Cl being trans to CO, and they seem too high in frequency to be due to Cl trans to P. The observations apparently eliminate VIII and IX from consideration, but they leave the nature of the isomerism obscure. We think that **5b** probably has structure X, and **5a** has structure IX, and we suggest that ranges of ν(RuCl) trans to various ligands[22] may overlap to a greater extent than previously recognized. It may be noted that the recent isolation of two isomeric *cis*-dicarbonyls of formula $RuCl_2(CO)_2\{P(C_6H_5)_3\}_2$, which have ν(CO) values very similar to those of **5a** and **5b**, has cast doubt on previous stereochemical assignments,[27] but unfortunately far-ir data for these complexes are not available. However, our assignments agree with those given by James and Markham.[27]

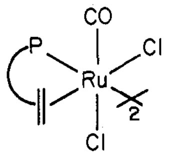
Ruthenium(II) complexes containing one bidentate SP ligand are obtained by heating hydrated ruthenium trichloride with 1.5–2 mol of SP per g-atom of Ru in 2-methoxyethanol in an atmosphere of carbon monoxide. This reaction gives a colorless, crystalline complex $RuCl_2(CO)_2(SP)$, **6**, which is poorly soluble in most organic solvents. Its ^{1}H nmr spectrum (Table II) shows the presence of bidentate SP, and its ir spectrum in the ν(CO) and ν(RuCl) regions (Table I) indicates that the carbonyl groups must be mutually cis and that the chlorine atoms are also mutually cis. We favor structure XI, in which the chlorine atoms are trans to coordinated olefin and to CO, respectively, in preference to XII, in which one of the chlorine atoms is trans to phosphorus. Both of the observed ν(RuCl) bands are too high in frequency for chlorine trans to phosphorus according to the previously cited ranges,[22] and the two strongly π-bonding ligands CO and olefin would probably prefer to be mutually cis. On heating in 2-methoxyethanol in the absence of carbon monoxide, **6** decomposes to a dimeric monocarbonyl complex $[RuCl_2(CO)(SP)]_2$, which can be isolated in two isomeric forms, **7a** and **7b**, which exhibit markedly different ir spectra in the ν(CO) and ν(RuCl) regions (Table I). The mass spectra of both isomers show highest mass peaks due to the species $[Ru_2Cl_3(CO)_2(SP)_2]^+$. The soluble isomer **7a** slowly isomerizes to **7b**, which is only slightly soluble in chloroform and dichloromethane, and is insoluble in all other organic solvents. The ^{1}H nmr spectrum of **7a** (Table II) shows the presence of bidentate SP, but the far ir spectra do not enable us to distinguish between the various possible isomeric chlorine-bridged complexes of which XIII is an example.



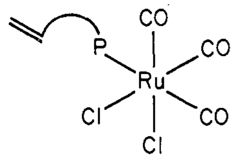
XI



XII



XIII



XIV

The reaction of $[RuCl_2(CO)_3]_2$ with SP (1 mol per g-atom of Ru) in refluxing benzene unexpectedly yields as the only product a tricarbonyl complex $RuCl_2(CO)_3(SP)$, **8**, which contains monodentate P-bonded SP, as shown by the ^{1}H nmr spectrum (Table II) and by the appearance of the characteristic bands due to olefinic (C–H) out-of-plane deformation modes in the ir spectrum (Table I). Complexes of this type have been isolated from the reaction of either $RuX_2(CO)_4$ (X = Br or I) or $RuCl_2(CO)$ (diene) with pyridine and substituted pyridines[3,28] but have not been found in analogous reactions involving tertiary phosphines (PR_3), which give the well-known di- and monocarbonyl complexes RuX_2-

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(24) M. A. Bennett and I. B. Tomkins, *J. Organometal. Chem.*, 51, 289 (1973).

(25) M. A. Bennett, E. J. Hann, and R. N. Johnson, unpublished work.

(26) M. A. Bennett, R. N. Johnson, and I. B. Tomkins, unpublished work.

(27) B. R. James and L. D. Markham, *Inorg. Nucl. Chem. Lett.*, 7, 373 (1971), and references cited therein.

(28) A. Trovati, A. Araneo, P. Uguagliati, and F. Zingales, *Inorg. Chem.*, 9, 671 (1970).

$(CO)_2(PR_3)_2$ and $RuX_2(CO)(PR_3)_3$.[21,22,29] Complexes $RuX_2(CO)_3\{P(C_6H_5)_3\}$ (X = Cl or I) have, however, been isolated by halogenation of $Ru(CO)_3\{P(C_6H_5)_3\}_2$.[30,31] The ir spectrum of **8** shows three strong ν(CO) bands and resembles the spectra of the analogous pyridine and triphenylphosphine complexes. Structure XIV, which has a fac arrangement of CO groups, seems most probable and is also consistent with the observation of two ν(RuCl) bands (Table I) which are in the range characteristic of CO trans to Cl in ruthenium(II) complexes. In refluxing 2-methoxyethanol, **8** loses CO to give initially **7a** which then isomerizes to **7b**. Carbonylation of this mixture in refluxing 2-methoxyethanol forms the dicarbonyl chelate SP complex **6**, and on addition of SP the soluble dicarbonyl complex, $RuCl_2(CO)_2(SP)_2$, **5b** is formed.

The results show that *o*-styryldiphenylphosphine forms a wide range of chelate olefin complexes with divalent ruthenium in which the element displays its usual sixfold, presumably octahedral, coordination. Recently we have also isolated chelate olefin complexes of general formula

$$(RuX_2(CO)\{o\text{-}(C_6H_5)_2PC_6H_4CH_2CH\overset{c}{=}CHCH_2C_6H_4P(C_6H_5)_2\text{-}o\}$$

$$(X = Cl\text{ or }Br)^{26}$$

in which the ligand bis-1,4-(*o*-diphenylphosphino)phenyl-*cis*-2-butene coordinates to divalent ruthenium *via* two phosphorus atoms and the cis double bond, and a single crystal X-ray study[32] of the dibromo complex has shown essentially octahedral coordination about the metal atom. The chelate complexes formed by these tertiary phosphines are the first well-characterized monoolefin complexes of divalent ruthenium. The complexes of SP are thermally stable and show no tendency to lose the tertiary phosphine under normal reaction conditions, although the coordinated double bonds can be displaced by carbon monoxide when two SP molecules are attached to the metal. This behavior can be contrasted with the reversible reaction of the five-coordinate complex $RhCl(SP)_2$ with CO to give $[Rh(CO)(SP)_2]^+Cl^-$ and the irreversible addition of CO to the planar cation $[Rh(SP)_2]^+$ to give five-coordinate $[Rh(CO)(SP)_2]^+$;[17,18] in neither case is displacement of the coordinated vinyl groups observed. These observations imply that the affinity of CO and tertiary phosphines for ruthenium(II) is greater than that of olefins such as ethylene, whereas for rhodium(I) the difference is less marked. In line with this conclusion is the fact that $RuCl_2\{P(C_6H_5)_3\}_4$ gives no isolable product with ethylene,[3] though it does react with CO to give $RuCl_2(CO)_2\{P(C_6H_5)_2\}_2$;[33] in contrast, $RhCl\{P(C_6H_5)_3\}_3$ reacts reversibly with ethylene to give $RhCl(C_2H_4)\{P(C_6H_5)_3\}_2$ and irreversibly with CO to give $RhCl(CO)\{P(C_6H_5)_3\}_2$.[34] Since the affinity of tertiary arsines and stibines for most transition metals is generally less than that of tertiary phosphines, a more promising approach to the preparation of ruthenium(II)–ethylene complexes might be to start with complexes of triphenylarsine or triphenylstibine. In this connection, it is worth noting that the rhodium(I) complexes $RhCl(C_2H_4)\{E(C_6H_5)_3\}_2$ (E = As or Sb), unlike the analogous triphenylphosphine complex, do not readily lose their coordinated ethylene in the presence of an inert gas.[35] Despite these differences, preliminary experiments suggest that the coordinated vinyl groups of $RuBr_2(SPAS)_2$, like those of $RuCl_2(SP)_2$, are readily displaced by carbon monoxide to give $RuBr_2(CO)_2(SPAS)_2$ [ir identification, ν(CO) 2060, 1996 cm^{-1} (Nujol)].

Acknowledgment: We thank Mr. C. Arandjelovic for some of the nmr spectra, Dr. R. Bramley for the CAT program used in obtaining ^{31}P nmr spectra, and Johnson-Matthey Co. (U.K.) for a loan of ruthenium chloride.

Registry No. $[RuCl_2(CO)_3]_2$, 22594-69-0; $RuCl_2(SP)_2$ (**1a**), 42934-11-2; $RuCl_2(SP)_2$, 42934-17-8; $RuBr_2(SP)_2$, 42934-12-3; $RuCl_2(SPAS)_2$, 42934-13-4; $RuBr_2(SPAS)_2$, 42934-14-5; $RuCl_2(CO)_2(SP)_2$ (**5a**), 42934-15-6; $RuCl_2(CO)_2(SP)_2$ (**5b**), 42934-16-7; $RuCl_2(CO)_2(SP)$, 42947-50-2; $[RuCl_2(CO)(SP)]_2$, 42947-51-3; $RuCl_2(CO)_3(SP)$, 42934-18-9.

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