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Hydrogenation and Coupling of Vinyl Groups in the Coordination Sphere of a Divalent Ruthenium Complex Formed by an Olefinic Tertiary Phosphine

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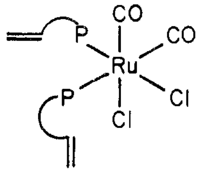
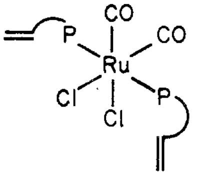
The complex $RuCl_2(CO)_2(SP)_2$ (I) (SP = *o*-styryldiphenylphosphine, *o*-$CH_2{=}CHC_6H_4PPh_2$), which contains monodentate P-bonded SP, reacts in boiling 2-methoxyethanol to give three new octahedral complexes of ruthenium(II), the structures of which have been deduced from ir and ^1H and ^{31}P NMR spectroscopic studies and in one case by a single-crystal X-ray diffraction study. The major product, $RuCl(CO)(o\text{-}CH_3CHC_6H_4PPh_2)(SP)$ (II), contains one bidentate SP moiety and a five-membered chelate ruthenium–carbon σ-bonded ring formed by addition of one hydrogen atom to coordinated SP. ^1H and ^{31}P NMR studies show that complex II in solution consists of an equilibrium mixture of two isomeric forms. Similar results are obtained for the derived dicarbonyl cation $[Ru(CO)_2(o\text{-}CH_3CHC_6H_4PPh_2)(SP)]^+$ (III). In each case, interconversion of the isomers was observed by NMR above ambient temperature and the rate of exchange was estimated from the spectra obtained. The isomerism is attributed to different orientations of the coordinated vinyl group. The second complex is $RuCl(CO)_2[o\text{-}Ph_2PC_6H_4CHCH_2CH(CH_3)C_6H_4PPh_2\text{-}o]$ (IV), in which the two vinyl groups of I have incorporated one hydrogen atom and coupled to give a tridentate PCP grouping containing fused five- and seven-membered chelate rings. The third complex, $RuCl(CO)(o\text{-}OHCCHC_6H_4PPh_2)(SP)$ (VII), which is formed in very low yield, is formally derived from II by oxidation of the methyl group to an aldehyde function. Carbonylation of II for 1 hr gives a mixture of IV with an isomer V, $RuCl(CO)_2[o\text{-}Ph_2PC_6H_4CH_2CHCH(CH_3)C_6H_4PPh_2\text{-}o]$, which differs from IV in that it contains two fused six-membered rings; i.e., the ruthenium–carbon σ bond is formed at the 2 instead of the 1 position of the butane chain. V can be prepared in a pure state by addition of hydrogen chloride to the ruthenium(0) complex of 1,3-bis[*o*-(diphenylphosphino)phenyl]-*trans*-1-butene, $Ru(CO)_2[o\text{-}Ph_2PC_6H_4CH{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o]$ (VI). V isomerizes to IV in boiling 2-methoxyethanol, possibly via an olefin hydride intermediate. Under forcing conditions I reacts with 2-methoxyethanol to give a mixture of IV and a complex of *o*-ethylphenyldiphenylphosphine, $RuCl_2(CO)_2(o\text{-}Ph_2PC_6H_4C_2H_5)_2$ (XV). The formation of II, IV, and XV is thought to involve reaction of I with 2-methoxyethanol to give intermediate ruthenium(II) hydride complexes.

We have shown[1] that (*o*-vinylphenyl)diphenylphosphine (*o*-styryldiphenylphosphine), *o*-$CH_2{=}CHC_6H_4PPh_2$ (abbreviated SP), forms stable, chelated octahedral olefin complexes with divalent ruthenium, e.g., $RuCl_2(SP)_2$, and that the coordinated vinyl groups of this complex are displaced by carbon monoxide to give isomers of $RuCl_2(CO)_2(SP)_2$ (Ia, Ib),



Ia



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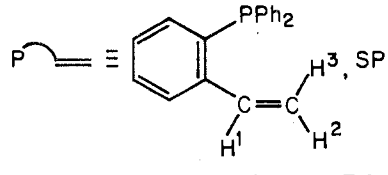


in which SP behaves as a monodentate, P-bonded ligand. [Note: the precise arrangement of ligands about ruthenium in Ia and Ib is not known with certainty. Those shown are considered the most likely (see ref 1).] We now report on reactions which isomers Ia and Ib undergo on prolonged heating in 2-methoxyethanol, some of which involve addition of hydrogen atoms and coupling of the uncoordinated vinyl groups. Coupling of coordinated and uncoordinated vinyl groups has previously been observed in ruthenium(0) complexes of SP.[2]

Experimental Section

Preparative, analytical, and spectroscopic procedures have been described previously.[1,2] Relative signs of ^1H–^1H coupling constants were determined by partial ^1H-decoupling experiments with simultaneous noise-modulated irradiation at the ^{31}P resonance frequencies. Analytical data are in Table I. The starting complex $RuCl_2(CO)_2(SP)_2$ was usually prepared in situ by carbonylation at 1 atm of a mixture of $RuCl_2(SP)_2$ isomers in refluxing 2-methoxyethanol, the product itself being an isomeric mixture.[1]

Preparations. Carbonylchloro[1-(*o*-diphenylphosphino)phenylethyl](*o*-styryldiphenylphosphine)ruthenium(II), $RuCl(CO)(o\text{-}CH_3CHC_6H_4PPh_2)(o\text{-}CH_2{=}CHC_6H_4PPh_2)$, II. A solution of Ia or Ib prepared by carbonylation of $RuCl_2(SP)_2$ (0.37 g, 5×10^{-4} mol) in 2-methoxyethanol (40 ml) was heated under reflux in a nitrogen atmosphere for 2 hr. Solvent was removed under reduced pressure on a rotary evaporator and the oily yellow residue was dissolved in dichloromethane (10 ml). The solution was filtered and methanol (40 ml) was added. After 24 hr, the supernatant liquid was decanted and the residual colorless crystalline product was washed with methanol and dried at 50–60° (10^{-3} mm) for 2 hr; yield 0.23 g (60%).

Dicarbonyl[1-(*o*-diphenylphosphino)phenylethyl](*o*-styryldiphenylphosphine)ruthenium(II) Tetrafluoroborate, $[Ru(CO)_2(o\text{-}CH_3CHC_6H_4PPh_2)(o\text{-}CH_2{=}CHC_6H_4PPh_2)]BF_4$, III. A solution of II (0.1 g) in dichloromethane (25 ml) was saturated with carbon monoxide and anhydrous silver tetrafluoroborate (0.05 g) was added. The mixture was stirred for 10 min and filtered to remove silver chloride. The solution was evaporated in vacuo to ca. 10 ml and treated with isopentane (30 ml), which precipitated a colorless microcrystalline solid. This was centrifuged, washed with isopentane, and dried in vacuo. The yield was almost quantitative.

Chlorodicarbonyl[1,3-bis[*o*-(diphenylphosphino)phenyl]-1-butyl]ruthenium(II), $RuCl(CO)_2[o\text{-}Ph_2PC_6H_4CHCH_2CH(CH_3)C_6H_4PPh_2\text{-}o]$, IV ("1-Butyl" Isomer). A solution of II (0.2 g) in refluxing 2-methoxyethanol (20 ml) was treated with carbon monoxide for 4–5 hr. The product precipitated as a colorless microcrystalline solid when the solution was set aside at room temperature for 48 hr. After decantation and washing with methanol, the complex was recrystallized from dichloromethane by addition of *n*-hexane; yield 0.145 g (70%).

IV was also prepared in 70–80% yield from the reaction of chlorotricarbonyl[1-(*o*-diphenylphosphino)phenylethyl]ruthenium(II), $RuCl(CO)_3(o\text{-}CH_3CHC_6H_4PPh_2)$ (0.1 g),[3] and an excess of SP (0.085 g) in refluxing 2-methoxyethanol (2 hr). Neither the "2-butyl"

Table I. Analytical Data and Selected Infrared Bands

Complex	% C		% H		% Cl		% P		ν(CO),[a] cm^{-1}	ν(RuCl),[a] cm^{-1}
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
$RuCl(CO)(o\text{-}CH_3CHC_6H_4PPh_2)(SP)$ (II)[b]	66.4	65.0	4.7	4.7	4.8	7.1	8.3	7.9	1926	290
$[Ru(CO)_2(o\text{-}CH_3CHC_6H_4PPh_2)(SP)]BF_4$ (III)	61.4	60.1	4.3	4.5			7.5	7.2	2024	
$RuCl(CO)_2[o\text{-}Ph_2PC_6H_4CHCH_2CH(CH_3)C_6H_4PPh_2\text{-}o]$ (IV)[c]	65.5	65.9	4.6	4.4	4.6	5.6	8.0	7.8	2025, 1960[d]	284[d]
$RuCl(CO)_2[o\text{-}Ph_2PC_6H_4CH_2CHCH(CH_3)C_6H_4PPh_2\text{-}o]\cdot 0.5CH_2Cl_2$ (V)	62.9	64.1	4.5	4.7	8.7	8.4	7.6	7.4	2025, 1960[d]	285[d]
$Ru(CO)_2[o\text{-}Ph_2PC_6H_4CH{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o]\cdot 0.5CH_2Cl_2$ (VI)	65.8	65.8	4.55	4.6			8.0	7.8	1972, 1912	
$RuCl(CO)(o\text{-}OHCCHC_6H_4PPh_2)(SP)\cdot 0.9CH_2Cl_2$ (VII)[e,f]	60.4	60.7	4.2	4.7	11.9	11.7	7.4	7.2	1965, 1665[g]	
$RuCl_2(CO)_2(o\text{-}Ph_2PC_6H_4C_2H_5)_2\cdot CH_2Cl_2$ (XV)[e]	57.8	58.3	4.5	5.1			6.9	6.7	2065, 1998	311, 284

[a] Measured in Nujol mulls; all bands quoted are strong or are of medium intensity. [b] C, Cl, and P analyses are consistent with the presence of ~0.25 mol of CH_2Cl_2/mol of complex, confirmed by ^{1}H NMR in C_6D_5Br. [c] ^{1}H NMR in $CDCl_3$ showed the presence of some residual CH_2Cl_2. [d] Measured in CsBr disks. [e] ^{1}H NMR showed presence of CH_2Cl_2 in approximate amounts shown. [f] Calcd for $RuCl(CO)(o\text{-}OHCCH{=}CC_6H_4PPh_2)(SP)\cdot CH_2Cl_2$: C, 60.5; H, 4.1; Cl, 12.5; P, 7.3. [g] ν(C=O) of aldehyde group.

isomer V (see below) nor II was detected even with shorter reaction times (<45 min). A similar experiment carried out in refluxing toluene (4 hr) gave only II (ir identification).

IV could also be obtained in 18% yield from the reaction leading to II and in 35% yield from the reaction of II with 2-methoxyethanol at 150° in a sealed tube (see below).

Carbonylation of II (0.2 g) in refluxing 2-methoxyethanol for ca. 1 hr and work-up as described above gave a product shown by its ^{1}H and ^{31}P NMR spectra to be an approximately 1:1 mixture of IV with the "2-butyl" isomer V; the latter has been synthesized independently (see below).

In one experiment, II was carbonylated in refluxing 2-methoxyethanol for 20 min. Solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. On addition of *n*-hexane, a small amount of a complex believed to be $[RuCl(CO)_2(o\text{-}CH_3CHC_6H_4PPh_2)]_2$ was precipitated. This was identified by its ir spectrum in the ν(CO) region [2068, 2016 cm^{-1} (CH_2Cl_2); 2066, 2010 cm^{-1} (Nujol)][3] and by its reaction with carbon monoxide in refluxing chloroform to give $RuCl(CO)_3(o\text{-}CH_3CHC_6H_4PPh_2)$ [ν(CO) 2112, 2058, 2020 cm^{-1} (CH_2Cl_2); 2110, 2052, 2018 cm^{-1} (Nujol)].[3] The supernatant liquid was evaporated to dryness and again redissolved in dichloromethane. Its ir spectrum showed the presence of large amounts of unreacted II, traces of IV and V, and some $RuCl(CO)_3(o\text{-}CH_3CHC_6H_4PPh_2)$. Carbonylation of II in refluxing toluene for 8 hr gave only $RuCl(CO)_3(o\text{-}CH_3CHC_6H_4PPh_2)$ (ir identification).

Dicarbonyl[1,3-bis[*o*-(diphenylphosphino)phenyl]-*trans*-1-butene]ruthenium(0), $Ru(CO)_2[o\text{-}Ph_2PC_6H_4CH{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o]$, Ru(CO)$_2$(1-BDPB), VI. Triruthenium dodecacarbonyl (0.1 g) and 1,3-bis[*o*-(diphenylphosphino)phenyl]-*trans*-1-butene (1-BDPB)[4] (0.27 g; Ru:1-BDPB = 1:1) were stirred in refluxing *n*-octane (25 ml) under nitrogen for 2 hr. After standing overnight, the precipitated solid was centrifuged off, dissolved in dichloromethane (10 ml), and treated with methanol (30 ml). The yellow-orange solid which precipitated was stirred with a few milliliters of ice-cold dichloromethane to give the pale yellow product which was dried in vacuo; yield 0.21 g (61%). Mass spectrum: *m/e* 734 [parent ion (M) for ^{102}Ru(CO)$_2$(1-BDPB)], 706 [M − CO], and 678 [M − 2CO].

Chlorodicarbonyl[1,3-bis[*o*-(diphenylphosphino)phenyl]-2-butyl]ruthenium(II), $RuCl(CO)_2[o\text{-}Ph_2PC_6H_4CH_2CHCH(CH_3)C_6H_4PPh_2\text{-}o]$, V ("2-Butyl" Isomer). A suspension of VI (0.07 g) in dichloromethane (10 ml) was treated with dry hydrogen chloride for 1 min. The solid dissolved rapidly giving a colorless solution. After flushing out the excess hydrogen chloride with a stream of nitrogen, the solution was evaporated to ca. 5 ml and treated with *n*-hexane (15 ml). Colorless crystals of V deposited over a period of 2 days. These were washed with *n*-hexane and dried in vacuo; yield 0.05 g (70%).

Carbonylchloro[α-formyl(*o*-diphenylphosphino)benzyl](*o*-styryldiphenylphosphine)ruthenium(II), $RuCl(CO)(o\text{-}OHCCHC_6H_4PPh_2)(o\text{-}CH_2CHC_6H_4PPh_2)$, VII. This compound was isolated in a preparation of II using a reaction time of 1.25 hr as follows. The supernatant liquid obtained after II had separated was evaporated to dryness under reduced pressure. The residue was redissolved in dichloromethane (10 ml) and the solution was chromatographed on a silica gel column (100–200 mesh) made up in *n*-hexane. The products were eluted with dichloromethane. The first fraction (ca. 40 ml) contained complex IV, which was isolated in 18% yield by evaporation to small volume and addition of *n*-hexane. The second fraction (10–15 ml) contained traces of II and IV and was discarded. The next 30–40 ml was collected, evaporated to ca. 5 ml under reduced pressure, and treated with *n*-hexane (5 ml). The colorless crystals of VII which deposited overnight were washed with *n*-hexane and dried in vacuo at room temperature; yield 0.022 g (5%), as solvate.

Dicarbonyldichlorobis[(*o*-ethylphenyl)diphenylphosphine]ruthenium(II), $RuCl_2(CO)_2(o\text{-}C_2H_5C_6H_4PPh_2)_2$, XV. A mixture of II (0.2 g) and 2-methoxyethanol (40 ml) was heated at 150° in a sealed tube under nitrogen for 5 hr. After cooling, the tube was opened and the yellow solution was taken to dryness on a rotary evaporator. The residue was dissolved in dichloromethane (10 ml), and methanol (10 ml) was added. After 24 hr the colorless crystals of XV were collected, washed with methanol, and dried in vacuo. The yield of 1:1 solvate with dichloromethane was 0.11 g (50%). Chromatography of the supernatant liquid on silica gel and recrystallization from dichloromethane–*n*-hexane gave IV in 35% yield. ^{1}H NMR of XV (CD_2Cl_2): δ 0.98 (t, CH$_3$, $J_{CH_2-CH_3}$ = 7.0 Hz), 2.25 (q, CH$_2$), 6.9–8.1 (aromatic). ^{31}P NMR (CH_2Cl_2): δ 29.9 (s, external H_3PO_4 reference).

Results and Discussion

When either of the two isomers of $RuCl_2(CO)_2(SP)_2$, Ia or Ib, or a mixture of both, is heated under reflux in 2-methoxyethanol for 1–1.5 hr under nitrogen, three new complexes can be isolated. The major product, formed in ca. 60% yield as a colorless crystalline solid, is identified on the basis of analytical and spectroscopic data (Table II) as $RuCl(CO)(o\text{-}CH_3CHC_6H_4PPh_2)(o\text{-}CH_2{=}CHC_6H_4PPh_2)$, i.e., an octahedral ruthenium(II) complex containing bidentate SP and a metal–carbon σ bond in a five-membered chelate ring (structure II). The infrared spectrum of II shows one ν(CO) band at 1926 cm^{-1} (Nujol) [1940 cm^{-1} (CH_2Cl_2 solution)] and one band assignable to ν(RuCl) at 290 cm^{-1} which is in the range noted[5] for Cl trans to CO in octahedral ruthenium(II) complexes. The proton NMR spectrum of II in $CDCl_3$ is broad and complex at 38°, and even with ^{31}P decoupling, which sharpens all signals to some extent, the only

Table II. ^1H and ^{31}P NMR Data for Complexes II, III, and VII

	^1H chem shifts^a					^1H coupling constants^b					
	δ_{CH_3}	δ_{CH}	δ_{H_1}	δ_{H_2}	δ_{H_3}	J_{CHCH_3}	J_{12}	J_{13}	J_{23}	$\delta_P{}^c$	$J_{PP}{}^d$
II^e	~1.5	~4.0	5.78 dd	~3.95	~3.45	?	10	13.5	?	55.8, 42.5	278
II(major isomer)^f	1.62	3.70	5.67	4.13	3.23	7	10	13.5	~1	53.0, 41.2	273
II(minor isomer)^f	0.60	4.1	5.78	3.19	3.99	7	10	14	~1	53.2, 39.1	278
II(time averaged)^g	1.30	3.95	5.79	3.95	3.55	7	10	13.5	<2	53.7, 40.7	276
III(major isomer)^h	1.10 d	3.9–4.0 d	6.18 dd	4.05 d	4.18 d	7.5	9.5	13.5	<1.5	48.8, 35.8^i	184^{i,j}
III(minor isomer)^h	1.35 d	3.9–4.0 d	6.45 dd	3.96 d	3.37 d	7.3	9.0	14.0	<1.5		
VII^e	9.27 d^k	4.72 d	5.70 dd	4.18 d	3.22 d	4.7^k	9.5	13.5	<1.5	47.5, 40.2	269^l

[a] In ppm downfield from internal TMS, measured with ^{31}P noise decoupling. Protons are numbered as shown in structure I. Abbreviations: d, doublet; dd, doublet of doublets. Aromatic resonances are multiplets in the range δ 6.9–8.1. [b] In Hz, ±0.5. [c] In ppm downfield from external 85% H_3PO_4, ±0.3 ppm. Positive shift is on low-field side. [d] In Hz, ±5. [e] ^1H NMR at 34° in CD_2Cl_2; ^{31}P NMR at 38° in CH_2Cl_2. [f] ^1H and ^{31}P NMR at −20° in $CDCl_3$. [g] ^1H and ^{31}P NMR at +60° in $CDCl_3$. [h] ^1H NMR at 34° in $CDCl_3$; ^{31}P NMR at 34° in $CHCl_3$. [i] ^{31}P NMR spectrum of minor isomer strongly overlaps that of major isomer (see text). [j] J_{P-H_3} = 2.0, 0 Hz for minor isomer. The other J_{HP}'s were difficult to assign, except that for each isomer of III, J_{PH_1} was ca. 1 Hz. [k] Aldehyde proton; coupling refers to J_{CHCHO}. [l] Other couplings (Hz): J_{PH_1} = 0, 2.0; J_{PH_2} = 0, 7.0; J_{PH_3} = 0, 3.0; J_{P-CHO} = 0, 0; J_{P-CH} = 4.5, 7.0. Phosphorus atoms could not be selectively decoupled to permit proper assignment.

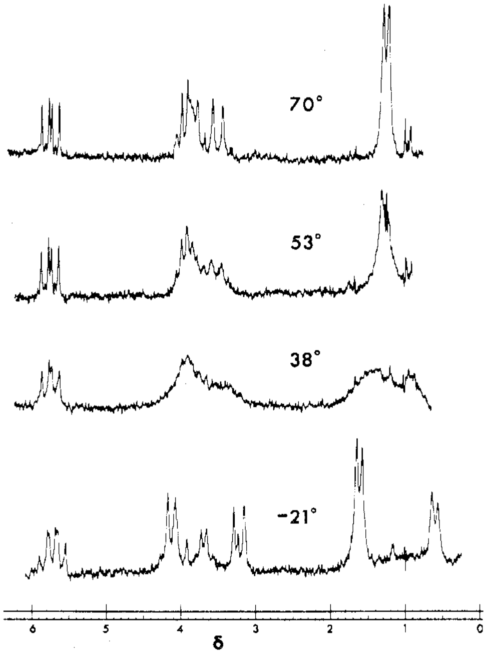
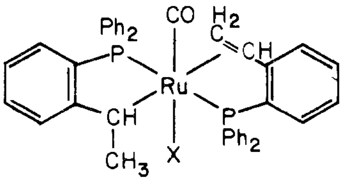


Figure 1. ^1H NMR spectra with ^{31}P decoupling of II in $CDCl_3$ at various temperatures. The beat signals at δ 1.0 are associated with the second harmonic of the 50-Hz electricity supply.



II, X = Cl
III, X = CO⁺

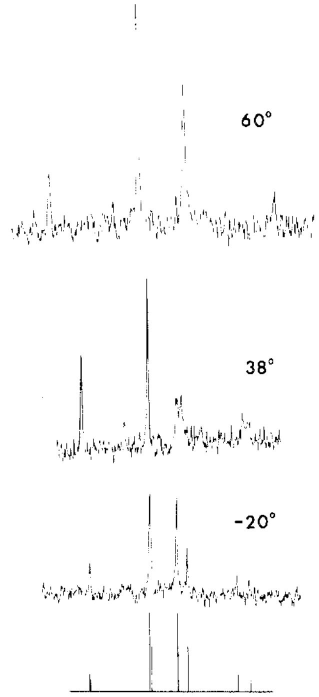


Figure 2. ^1H-decoupled ^{31}P NMR spectra at 24.29 MHz of II in $CHCl_3$ at various temperatures. The spectral widths of these spectra were not the same.

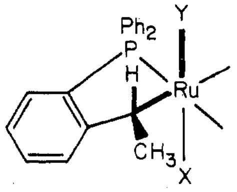
well-resolved signal (apart from aromatic resonances) is a doublet of doublets at δ 5.78 which is typical of the α proton (H^1) of the coordinated vinyl group of chelate SP. The remainder of the spectrum consists of broad bands centered at δ 4.1, 3.5, and 1.5. On cooling, the latter three signals separate and sharpen and the signal at δ 5.78 first broadens and on further cooling separates and sharpens. At −20° a well-resolved "frozen" spectrum is obtained in which signals of two isomers in a ratio of ca. 2:1 are observed. For each isomer there is one methyl doublet and one mutually coupled set of three vinyl resonances. The chemical shifts of the latter are upfield of those of free SP, and the cis- and trans-proton coupling constants are smaller than those of free SP, as expected for a coordinated vinyl group. On heating above 38° the signals sharpen and become resolved until at 70° there is obtained a well-resolved fully time-averaged spectrum due to rapid exchange between the two isomers observed at low temperature (see Figure 1). At 38° the ^{31}P NMR spectrum of II in $CHCl_3$ consists of two overlapping AB quartets of approximately equal intensity, the A spectra being nearly coincidental and appearing as two sharp peaks and the B spectra being shifted by about 1 ppm and appearing as four broad peaks (Figure 2). This result clearly shows that at 38° a solution of II contains approximately equal amounts of two isomers which are undergoing intramolecular exchange at a slow to intermediate rate on the NMR time scale. The magnitude of $^2J_{PP}$ (Table II) shows that each isomer contains mutually trans phosphorus atoms. At +60° in $CHCl_3$ the ^{31}P spectrum consists of a single time-averaged AB quartet which is still slightly broadened by the exchange process. At −20° in $CHCl_3$ the isomer ratio was ca. 2:1 (Figure 2) in agreement with the proton spectrum, whereas in CH_2Cl_2 the ratio was ca. 3:1.

It is evident from the above discussion that the position of equilibrium is slightly dependent on both temperature and solvent. Owing to the temperature dependence, the activation energy for the exchange process cannot be obtained accurately, but it can be estimated by line shape analysis if a fixed isomer population is assumed. The line shapes at different temperatures (in the range 25–55°) of the ^{31}P spectrum (^{1}H decoupled; isomer ratio assumed to be 55:45) and of the methyl and vinyl regions of the proton spectrum (^{31}P decoupled; isomer ratio assumed to be 65:35) all yielded rates corresponding to a free energy of activation $\Delta G^{\ddagger}(44°) = 15.2 \pm 0.5$ kcal/mol.

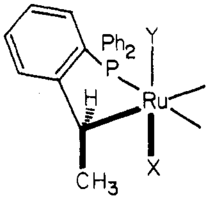
Before discussing the nature of the isomers, it is convenient to consider the NMR spectra of the derived cationic dicarbonyl complex $Ru(CO)_2(o\text{-}CH_3CHC_6H_4PPh_2)(o\text{-}CH_2{=}CH\text{-}C_6H_4PPh_2)]BF_4$, III, which is formed from II by treatment with silver tetrafluoroborate in an atmosphere of carbon monoxide. III shows a single, very sharp band due to $\nu(CO)$ at 2024 cm^{-1} indicative of mutually trans carbonyl groups and a broad absorption typical of BF_4^- at 1050 cm^{-1}. The proton NMR spectrum at room temperature shows two well-resolved methyl doublets ($J = 7.0$–7.5 Hz) in an approximate ratio of 3:2 and two sets of vinyl resonances characteristic of coordinated SP (Table II). Above room temperature the methyl doublets broaden and eventually coalesce at about 70°. The broad resonance sharpens at still higher temperatures to give a single doublet at about 90°, and on cooling to room temperature the original spectrum is obtained. The activation energy for this intramolecular exchange was estimated by line-shape analysis, $\Delta G^{\ddagger}(70°) \approx 17.7 \pm 0.3$ kcal/mol. The ratio of isomers did not appear to be temperature or solvent dependent. The vinyl resonances also coalesce and sharpen into one time-averaged set over the same temperature range. The ^{31}P NMR spectrum at room temperature consists of two AB quartets which overlap so much that individual parameters for the two isomers could not be extracted; "average" data are given in Table II. However, the magnitude of $^{2}J_{PP}$ shows that both isomers of III, like those of II, contain mutually trans phosphorus atoms.

There are a number of features which could be responsible for the observed isomerism.

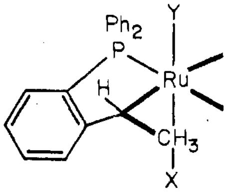
(1) Interchange of H and CH_3 on the asymmetric σ-bonded carbon atom would give rise to isomers in the case of II because of the different axial ligands CO and Cl. However this isomerism is clearly not possible for III and moreover we would not expect isomers of this type to exchange readily. If the formation of II is thermodynamically controlled, the methyl group and the chlorine atom will probably be as far apart as possible (IIIa–IIIc; X = CO, Y = Cl).



IIIa



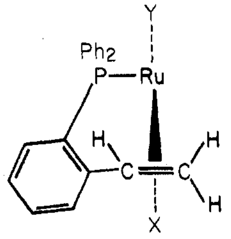
IIIb



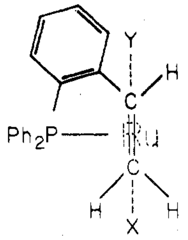
IIIc

(2) The five-membered σ-bonded chelate ring has, in principle, two puckered conformations which have the methyl group pseudoequatorial (IIIa) and pseudoaxial (IIIb). The second conformation is adopted in the complex $Mn(CO)_4[o\text{-}CH_3CHC_6H_4PPh_2]$,[6] whereas in the complex $RuBr(CO)_3[o\text{-}CH_3CHC_6H_4PPh_2]$[3] a distorted form of IIIa is observed, i.e., IIIc (X = Br, Y = CO), presumably as a consequence of steric interaction between the methyl group and the bulky bromine atom. We would however expect one conformation to predominate in a particular complex, and the barriers between five-membered ring conformations of similar energy are usually small.

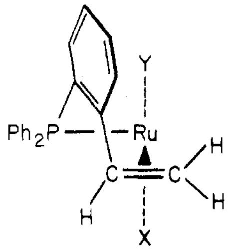
(3) A more likely explanation of isomerism and exchange in both II and III is an intramolecular reorientation of the coordinated vinyl group. The vinyl group of one isomer might be in the plane containing it and the phosphorus atoms, and the vinyl group of the other isomer might be at right angles to that plane, as shown diagrammatically in IIId and IIIe. The infrared spectra in the $\nu(CO)$ region of the octahedral complexes $M(CO)_4(SP)$ (M = Mo, W) strongly suggest that rotational isomers of this type are present in solution, although the interconversion is apparently too fast to be studied by NMR between +34 and −90°.[7,8] Two possible isomers arise from each of these orientations as a consequence of the asymmetry of the rest of the molecule,[9] i.e. IIId and IIIf *or* IIIe and IIIg. The mechanism of exchange between IIId and IIIf (or between IIIe and IIIg) would involve cleavage of the metal–olefin bond, thus allowing bonding to either "face" of the olefin. It is also possible that both bond breaking and 90° flipping are occurring, the latter being fast on the NMR time scale, as in $M(CO)_4(SP)$ (M = Mo, W), i.e., (IIId, IIIe) $\rightleftharpoons$ (IIIf, IIIg).



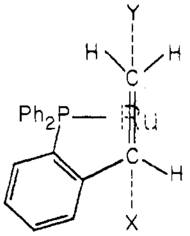
IIId



IIIe



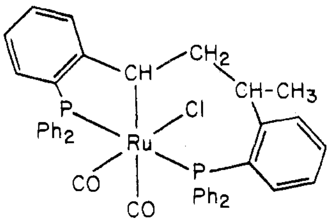
IIIf



IIIg

[Note that for complex III (X = Y = CO), IIId and IIIe do *not* become equivalent to IIIf and IIIg, respectively, owing to the presence of the asymmetric σ-bonded carbon in the $Ru\{o\text{-}CH_3CHC_6H_4PPh_2\}$ ring (not shown for clarity).] We can eliminate any mechanism involving rotation about the double bond since the cis and trans ^{1}H–^{1}H couplings do not become time averaged at high temperature. The high barrier observed compared with that in the $M(CO)_4(SP)$ complexes leads us to prefer the bond-breaking mechanism.

Chromatography of the supernatant liquid which remains after removal of II yields two complexes IV and VII in yields of 18% and ≤5%, respectively. The first of these (IV) is



IV

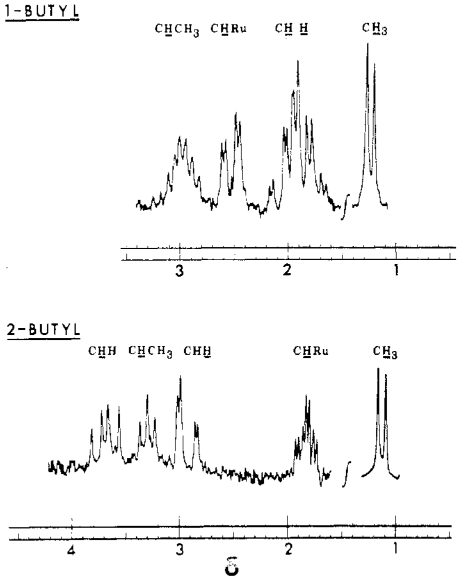


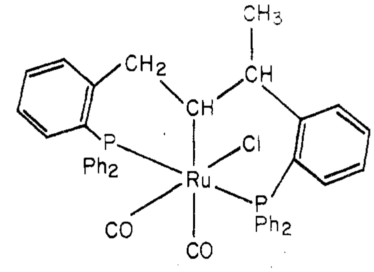
Figure 3. Partial ^1H NMR spectra with ^{31}P-decoupling of isomeric complexes IV ("1-butyl"; $-CH(Ru)-CH_2-CH(CH_3)-$) and V ("2-butyl"; $-CH_2-CH(Ru)-CH(CH_3)-$) in CD_2Cl_2-TMS. The methyl doublet was recorded at reduced amplitude in each case.

obtained in better yield by treatment of II with carbon monoxide (1 atm) in refluxing 2-methoxyethanol for 4 hr or by heating $RuCl(CO)_3[o\text{-}CH_3CHC_6H_4P(C_6H_5)_2]$ with an excess of SP in the same solvent. The latter complex is available from the reaction of $Ru(CO)_3(SP)$ with HCl.[3] IV is a colorless solid which shows two strong ν(CO) bands, typical of a *cis*-dicarbonyl, at 2025 and 1962 cm^{-1} (CsBr disk) and a band of 284 cm^{-1} tentatively assigned to ν(RuCl) (Cl trans to CO). The proton NMR spectrum (Figure 3) shows a doublet at δ 1.23 (J = 6.7 Hz) due to the presence of a $CHCH_3$ grouping, and partial proton-decoupling experiments on the remaining resonances (with simultaneous noise-modulated irradiation at the ^{31}P resonance frequency) establish the relative signs of most of the $^1H-^1H$ couplings (Table III). Geminal $^1H-^1H$ couplings are, except in a few special cases, negative, and vicinal $^1H-^1H$ couplings are generally positive. Thus for IV there is only one pair of geminal protons the coupling constant of which is typical of a methylene group adjacent to two sp^3-hybridized carbon atoms.[10] These data are in accord with the presence of a four-carbon chain $-CH(Ru)-CH_2-CH(CH_3)-$, and we suggest the octahedral structure IV, $RuCl(CO)_2[o\text{-}Ph_2PC_6H_4CHCH_2CH(CH_3)C_6H_4PPh_2\text{-}o]$, containing a tridentate PCP donor group. Molecular models suggest that the phosphorus atoms of this tridentate unit must be mutually trans, and this is confirmed by the observation of an AB quartet in the ^{31}P NMR spectrum with a large value of $^2J_{PP}$ (Table III).

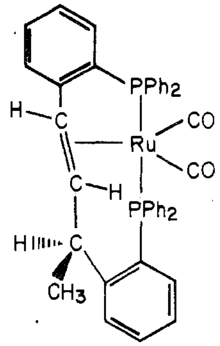
Table III. ^1H and ^{31}P parameters for Complexes IV and V[a]

	$(Ru)CH_BCH_CH_DCH_A$-(CH_3)(IV)		$CH_AH_CCH_D(Ru)$-$CH_B(CH_3)$(V)	
	δ	J_{HH} and J_{PP}	δ	J_{HH} and J_{PP}
CH_3	1.23	A-CH_3 6.7	1.14	B-CH_3 7.0
H_A	2.97	AB 0; AC +10.5 AD +4.8	3.66	AB 0; AC −16.0 AD +9.5
H_B	2.51	BC +3.8; BD +13.0	3.30	BC 0; BD 7.0
H_C	2.00	CD −13.5	2.95	CD +2.5
H_D	1.82		1.81	
P_A	52.1	P_AP_B 295[b]	60.0	P_AP_B 291[c]
P_B	26.6		36.9	

[a] Spectra run at 34° in CD_2Cl_2-TMS. Four chain protons are labeled A, B, C, and D in order of increasing field strength. Relative signs of coupling constants determined by $^1H\{^1H\}$ partial decoupling experiments with ^{31}P noise decoupling. Where not indicated, signs could not be determined. See also footnotes *a–d* of Table II. [b] Other couplings (Hz): $J_{P-H_A} \approx 1-2$; $J_{P-H_B} = 1, 9$; $J_{P-H_C} \approx 1$; $J_{P-H_D} \approx 1$. [c] P–H couplings could not be obtained accurately but are ≤2 Hz to each proton.



V

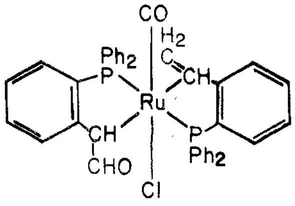


VI

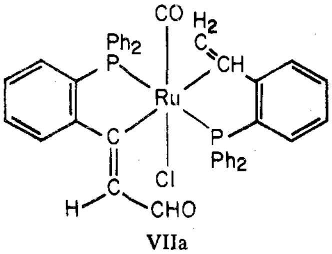
If complex II is carbonylated in refluxing 2-methoxyethanol for ca. 1 hr, a colorless crystalline compound can be isolated which is identical with IV in the ν(CO) region of the ir spectrum. The proton NMR spectrum shows that this compound is in fact an approximately 1:1 mixture of IV with an isomer V, which shows a methyl doublet at δ 1.14 (J = 7.0 Hz). On prolonged refluxing in 2-methoxyethanol V is entirely converted into IV. We have obtained V in a pure state as follows. On heating excess *o*-styryldiphenylphosphine with rhodium trichloride in 2-methoxyethanol, a rhodium(I) complex containing a tridentate olefinic ligand 1,3-bis[*o*-(diphenylphosphino)phenyl]-*trans*-1-butene (1-BDPB) is formed, viz., $RhCl[o\text{-}Ph_2PC_6H_4CH{=}CHCH(CH_3)C_6H_4PPh_2\text{-}o]$, and the ligand can be displaced from this complex by treatment with sodium cyanide.[4] Reaction of 1-BDPB with $Ru_3(CO)_{12}$ in refluxing *n*-octane gives the complex $Ru(CO)_2$(1-BDPB) (VI), which shows two ν(CO) bands in its ir spectrum (Table I) and a parent ion in its mass spectrum together with ions corresponding to the loss of two carbonyl groups. Unfortunately the complex is insufficiently soluble in the usual solvents for its NMR spectrum to be examined, but the similarity of the ν(CO) values to those of the known, five-coordinate complex $Ru(CO)_2(SP)_2$ (1978, 1917 cm^{-1} in cyclohexane)[2] supports a trigonal-bipyramidal structure VI with the coordinated olefin lying in the equatorial plane. The olefinic group is readily protonated by dry hydrogen chloride in dichloromethane to give the chelate alkyl compound V, the proton NMR spectrum of which (Figure 3, Table III) shows evidence of a $CHCH_3$ grouping as was found for IV. The relative signs of the $^1H-^1H$ couplings again showed only one geminal coupling, in this case −16.0 Hz. This value we regard as excellent evidence for the presence of a benzyl group, since a methylene function adjacent to an sp^2-hybridized carbon atom generally has $|J_{gem}| \approx$ 16–18 Hz.[10] These data suggest that V contains the unit $-CH_2-CH(Ru)-CH(CH_3)-$; i.e., V is $RuCl(CO)_2[o\text{-}Ph_2PC_6H_4CH_2CHCH(CH_3)C_6H_4PPh_2\text{-}o]$. The ir spectra of IV and V in the ν(CO) region are essentially the same, as also are their far-ir spectra. The ^{31}P NMR spectrum of V (Table III) indicates that the phosphorus atoms are mutually trans, so that the overall stereochemistry of IV and V is the same, with the two carbonyl groups being trans to Cl and σ-bonded carbon.

We refer to IV and V as the "1-butyl" and "2-butyl" isomers, respectively.

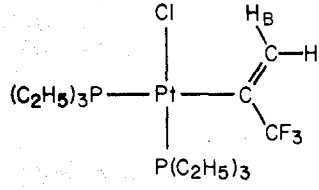
The third complex which can be isolated in low yield from the decomposition of $RuCl_2(CO)_2(SP)_2$ in 2-methoxyethanol shows one strong terminal ν(CO) band at 1965 cm^{-1} and a strong band at 1665 cm^{-1}. In addition to aromatic resonances and three resonances characteristic of chelated SP, there are two mutually coupled resonances at δ 4.72 and 9.27 in the proton NMR spectrum (Table II). The former is a multiplet which collapses to a sharp doublet on ^{31}P noise decoupling; the latter is a sharp doublet (J = 4.7 Hz) which shows no coupling to phosphorus and which must be assigned to the proton of an aldehyde group. The large P–H coupling to the former proton (J = 7.0 Hz) suggests that this proton may be attached to a carbon atom which is σ bonded to the metal atom as part of a chelate ring, i.e., that the complex is $RuCl(CO)(\textit{o}\text{-}OHCCHC_6H_4PPh_2)(\textit{o}\text{-}CH_2{=}CHC_6H_4PPh_2)$, derived formally from II by oxidation of the methyl group to an aldehyde function (structure VII). It is noteworthy that the major isomers of II and VII have almost identical chemical shifts and coupling constants for the vinyl protons; surprisingly, however, there was no evidence of exchange or of a second isomer of VII from room temperature to −90° in CD_2Cl_2. However, on the basis of spectroscopic data alone, we cannot eliminate an alternative structure containing a *cis*-α,β-unsaturated aldehyde grouping (structure VIIa) which could be responsible for the band at 1665 cm^{-1} in the infrared region.[11] The two alternatives differ by only one carbon atom and analysis does not distinguish between them, particularly as the complex contains firmly held dichloromethane of crystallization which need not be present in stoichiometric proportion. Moreover, in the vinylplatinum(II) complexes VIII–X, substantial four-bond P–H couplings to β-vinyl protons are observed,[12–14] so that the signal at δ 4.72 could be assigned to the β-vinyl proton of structure VIIa. Single-crystal X-ray diffraction analysis[15] has, however, shown that the structure is VII, the phosphorus atoms being mutually trans; this feature is also evident from the large value of $^2J_{PP}$ observed in the ^{31}P NMR spectrum (Table III). Surprisingly, we have been unable to locate a band due to ν(RuCl) in the 300-cm^{-1} region of the infrared spectrum.



VII

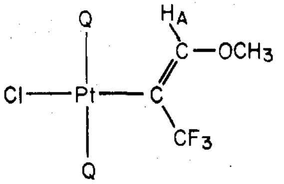


VIIa



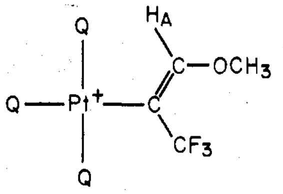
$^4J_{P\text{-}H_A} = 17$ Hz
$^4J_{P\text{-}H_B} = 9$ Hz[12]

VIII



$^4J_{P\text{-}H_A} = 1.7$ Hz[13]
[Q = $P(CH_3)_2Ph$]

IX

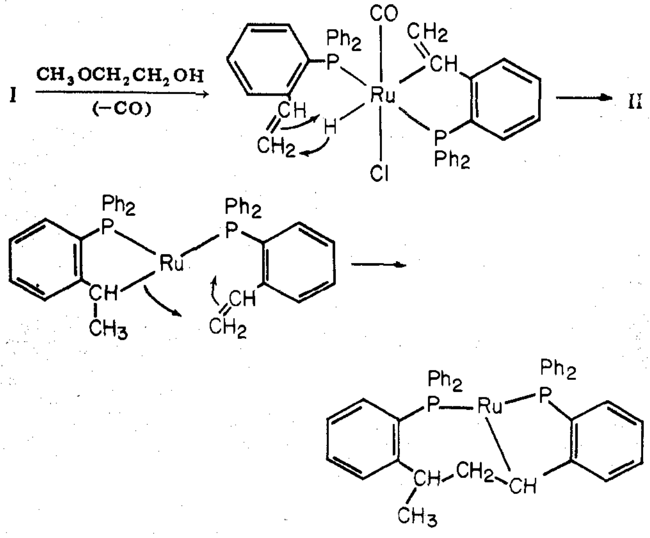


$^4J_{P\text{-}H_A}$(cis) = 2.2 Hz
$^4J_{P\text{-}H_A}$(trans) = 4.6 Hz[14]
[Q = $P(CH_3)_2Ph$]

X

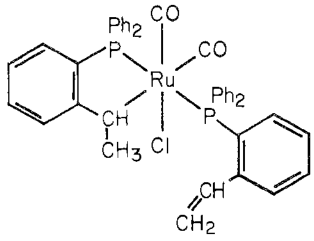
Although no detailed mechanism for the formation of the complexes can be given at present, the fact that metal–carbon σ-bonded complexes are generated from chloro complexes suggests that ruthenium(II) hydrides are involved. It is known that SP reacts with $MnH(CO)_5$[16] and with $PtHCl(PPh_3)_2$[17] to give chelate complexes containing the five-membered ring $MCH(CH_3)C_6H_4PPh_2\text{-}\textit{o}$, and the reaction of chlorides of ruthenium or osmium with tertiary phosphines in the presence of ethanolic alkali or high-boiling alcohols can be used to prepare hydridocarbonyls of these elements, e.g., $RuHCl(CO)(PEt_2Ph)_3$ from $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ and ethanolic potassium hydroxide[18] and $OsHCl(CO)(PPh_3)_3$ from ammonium hexachloroosmate(IV), triphenylphosphine, and 2-methoxyethanol.[19] The hydride and carbonyl ligands may be formed via intermediate alkoxy complexes. Thus a plausible route to II could involve loss of CO and replacement of a chloride ligand in I by hydride, giving complex XI (Scheme I); the hydride could then transfer to the free vinyl group. Alternatively, the hydride could transfer to the coordinated vinyl group with the free vinyl group taking up the vacated coordination position; an intermediate with hydride cis to coordinated olefin is suggested for this route. Formally the coupled product IV (the 1-butyl isomer) is derived by

Scheme I. Insertion Reactions of Ruthenium(II) Complexes of SP[a]



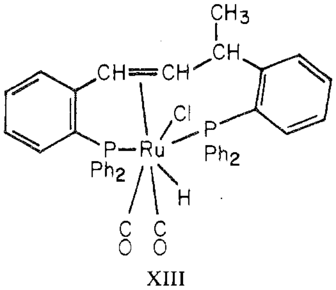
[a] Ancillary ligands omitted for clarity.

"insertion" of the vinyl group of SP into the metal–carbon σ bond of the five-membered ring $\overline{\mathrm{RuCH(CH_3)C_6H_4PPh_2}}$-*o* (Scheme I), but we cannot at present offer any convincing explanation of how and why IV and the 2-butyl isomer V are formed under particular circumstances and particularly why the presence of 2-methoxyethanol is crucial for coupling to occur; neither toluene nor ethanol is effective. Thus, if $\overline{\mathrm{RuCl(CO)_3(}o\mathrm{\text{-}CH_3CHC_6H_4PPh_2)}}$ is heated in toluene with 1 mol of SP, the only reaction observed is displacement of two CO groups giving II. This reaction is reversed by treatment of II with carbon monoxide in refluxing toluene. Both reactions could reasonably be expected to proceed via an intermediate XII containing P-bonded monodentate SP, yet in the presence of 2-methoxyethanol the forward reaction carried out for 2 hr yields IV exclusively, while the back-reaction yields a mixture of IV and V. In the second case it is uncertain whether V is formed first and subsequently isomerizes to IV or whether the two isomers are formed independently. Neither in the first case nor in the reaction of Ia or Ib with 2-methoxyethanol have we been able to detect V as an intermediate, even though its isomerization could not have been complete under the reaction conditions, so we suspect that IV and V are formed from different precursors. The nature of these precursors is not known at present.



XII

It is interesting that V is formed by addition of the proton to the α-carbon atom of the coordinated olefinic group in $\mathrm{Ru(CO)_2}$(1-BDPB) (VI), the metal–carbon σ bond being formed at the β-carbon atom, since the addition of hydrogen halides to $\mathrm{M(CO)_3(SP)}$ (M = Fe or Ru) occurs in the opposite sense.[3] It is noteworthy that V, which contains two fused six-membered chelate rings, is thermodynamically less stable than IV, which contains fused five- and seven-membered rings, and examination of models does suggest that IV is sterically the less strained of the two isomers. The isomerization probably proceeds via a hydridoolefin complex XIII; cf. the isomerizations of secondary to primary alkyl groups observed in iridium(III) and gold(III) complexes.[20,21]



XIII

The origin of the aldehyde complex VII is also unknown. It can only be isolated in low yields (≤5%) during the first 1 hr of reaction and does not appear to survive reaction periods greater than this. Once isolated, however, it is unreactive toward refluxing 2-methoxyethanol. There was no improvement in yield of VII if water (10% by volume) was added to the reaction mixture and/or if the reaction was done in the presence of air. An attempt to prepare VII by oxidation of the $\mathrm{CH_3}$ group of II with chromyl chloride led only to complete degradation. Since it seemed possible that a π-bonded formyl or acyl complex might be a precursor to VII, the reaction of Ia or Ib with SP was tried using *n*-butyraldehyde as solvent,[22] but no well-defined complexes could be isolated. A possibility which remains to be tested is that VII arises by some ruthenium(III)- or -(IV)-promoted oxidation of one of the vinyl groups of Ia or Ib to give a $\mathrm{CH_2CHO}$ group (cf. the palladium(II) chloride promoted oxidation of terminal olefins to aldehydes or ketones[23]), which then eliminates HCl at the internal carbon atom to form the Ru–C chelate σ-bonded ring. However, the addition of a small amount of commercial hydrated ruthenium trichloride to the reaction mixture did not improve the yield of VII.

In an attempt to improve the yield of the aldehyde complex VII, complex II was heated to 150° in 2-methoxyethanol in a sealed tube for 3 hr. The only products isolated were the coupled product IV (1-butyl isomer) and a new *cis*-dicarbonyl complex XV, which shows two ν(RuCl) absorptions in the ir spectrum but has no bands characteristic of a vinyl group. The proton NMR spectrum shows no vinyl resonances but does show a 1:3:3:1 quartet and a 1:2:1 triplet (J = 7.0 Hz) typical of an ethyl group. The compound thus appears to be an octahedral ruthenium(II) complex $\mathrm{RuCl_2(CO)_2(}o\mathrm{\text{-}Ph_2PC_6H_4C_2H_5)_2}$ containing (*o*-ethylphenyl)diphenylphosphine, formed by hydrogenation of the vinyl residues of SP. The hydrogen must come from 2-methoxyethanol, but the organic oxidation product has not been identified.

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Registry No. I, 55399-46-7; II, 55319-61-4; III, 55319-63-6; IV, 55319-64-7; V, 55319-65-8; VI, 55319-66-9; VII, 55319-67-0; XV, 55319-68-1; $\overline{\mathrm{RuCl(CO)_3(}o\mathrm{\text{-}CH_3CHC_6H_4PPh_2)}}$, 55399-47-8; $\mathrm{Ru_3(CO)_{12}}$, 15243-33-1.

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Thermal and Light-Induced Decomposition of Azido(bis-2,2'-bipyridine) Complexes of Ruthenium(III)

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The ruthenium(II) complexes $Ru(bipy)_2(N_3)_2$ (bipy is 2,2'-bipyridine) and $Ru(bipy)_2(L)(N_3)^+$ (L is acetonitrile or pyridine) are oxidized rapidly to ruthenium(III) either electrochemically or chemically, using Br_2 or Ce(IV). The ruthenium(III) complexes undergo thermal and light-induced decomposition reactions in acetonitrile in which *net* azide → metal electron transfer occurs

$$CH_3CN + Ru(bipy)_2(N_3)_2^+ \xrightarrow[\text{room temp}]{h\nu \text{ or}} Ru(bipy)_2(CH_3CN)N_3^+ + {}^3/_2N_2$$

The results of a series of kinetic studies are consistent with either rate-determining intramolecular electron transfer ($N_3^- \rightarrow Ru(III)$) or metal–nitrene formation. Gas evolution studies in the presence of acrylamide have shown that free azide radicals N_3^0 do not appear as intermediates in either the thermal or light-induced decomposition reactions of $Ru(bipy)_2(N_3)_2^+$. No evidence for dinitrogen complexes as intermediates has been found in solution, but infrared evidence has been obtained for the appearance of an intermediate dinitrogen complex at a low steady-state level in the solid-state decomposition of $[Ru(bipy)_2(N_3)_2]Br$.

Metal azide complexes commonly undergo thermal and/or light-induced decomposition reactions. The mechanistic details of the decomposition reactions in solution have been elucidated to a considerable degree recently by the use of flash photolysis techniques[2,3] and the results of both product isolation studies and of scavenging experiments for intermediates.[3-10]

For the systems which have been studied, it appears that strong, one-electron oxidants (e.g., Co(III),[11] Mn(III)[12]) react with N_3^- to give azide radicals, N_3^0, and the reduced form of the oxidant. Azide radicals are also produced in the light-induced decomposition of Co(III)[2,4] and of other metal azide[5,13] complexes. On the other hand, for the thermal decomposition reactions of ruthenium(III) azides[6,10] and the thermal and light-induced reactions of iridium(III) azides,[3,7,8] evidence has been obtained for the appearance of intermediate metal–nitrene complexes, e.g., $Ru(NH_3)_5NH^{3+}$. In the ultraviolet-catalyzed decomposition of $Rh(NH_3)_5N_3^{2+}$, evidence has been found for simultaneous paths involving both N_3^0 and metal–nitrene formation.[9]

We have prepared a series of azidobis(2,2'-bipyridine) complexes of ruthenium(II) and have found that they can be rapidly oxidized to the corresponding ruthenium(III) complexes either chemically or electrochemically. The ruthenium(III) complexes once formed undergo both thermal and light-induced decomposition reactions involving the bound azide group. We have been able to study the thermal reactions in some detail since they are amenable to a kinetic investigation.

Experimental Section

Measurements. Ultraviolet–visible spectra were recorded on Cary Model 14, Cary Model 17, Unicam Model SP-800B, or Gilford Model 240 spectrophotometers. Infrared spectra were obtained using a Perkin-Elmer Model 421 spectrophotometer. All electrochemical measurements were made at platinum electrodes vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2° and are uncorrected for junction potentials. In all electrochemical experiments, standard three-electrode operational amplifier circuitry was used as previously described,[14] or a Princeton Applied Research Model 173 Potentiostat/Galvanostat was used for potential control and current measurements with a Princeton Applied Research Model 175 Universal Programmer as a wave form generator for voltammetry and cyclic voltammetry experiments. Voltammograms and slow scan rate cyclic voltammograms were recorded on a Hewlett-Packard Model 7004B X-Y recorder. Fast scan rate cyclic voltammograms were obtained from photographs of the trace of a Tektronix Model 564B storage oscilloscope. Values of n, where n is the total number of electrons transferred in an exhaustive electrolysis at constant potential, were calculated after measuring the total area under current vs. time curves for the complete reaction. Reactions were judged to be complete when the current had fallen below 1% of its initial value.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[15] recrystallized three times from hot ethanol–water mixtures, and vacuum dried at 80° for 12 hr. Acetonitrile (MCB "Spectrograde") for use in electrochemical experiments was dried over Davison 4-Å molecular sieves before use. Dichloromethane (Fisher "Spectranalyzed") was used without further purification. Pyridine (Reagent Grade) was purified by distillation from KOH. Water was deionized and redistilled from alkaline $KMnO_4$. The complexes $Ru(bipy)_2Cl_2{\cdot}2H_2O$ and $[Ru(bipy)_2(NO)py](PF_6)_3$ were prepared as previously described.[16] Tetraphenylarsonium azide was prepared by the method of Bosnich and Dwyer.[17] All other solvents and chemicals were of commercially available reagent or spectrograde quality and were used without further purification.

Preparation of Compounds. All elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

***cis*-Ru(bipy)$_2$(N$_3$)$_2$·H$_2$O.** $Ru(bipy)_2Cl_2{\cdot}2H_2O$ (1.61 g, 3.09 mmol) was suspended in 35 ml of H_2O containing 3.00 g of NaN_3 (46 mmol). The mixture was heated to reflux under nitrogen for 1 hr with stirring. Upon cooling deep purple crystals formed which were collected by filtration, washed with water, and air-dried. The product was then dried overnight in a vacuum desicator over Drierite; 88% yield. Anal. Calcd for $RuC_{10}H_{18}N_{10}O$: C, 46.60; H, 3.52; N, 27.17. Found: C, 46.11; H, 3.70; N, 26.25.

[Ru(bipy)$_2$(N$_3$)(py)](PF$_6$)·H$_2$O (py is Pyridine). $Ru(bipy)_2(N_3)_2{\cdot}H_2O$ (185 mg, 0.346 mmol) was dissolved in about 25 ml of pyridine. A concentrated solution of Br_2 in acetonitrile (0.173 mmol), 0.39-ml total volume) was added with stirring. The solution immediately turned green and was allowed to stand in the dark at room temperature with stirring for ~15 hr. The solution gradually turned from green to red-brown. The product was then precipitated by