

Olefinic Tertiary Phosphine Complexes of Iron and Ruthenium. Coupling and Dehydrogenation of Vinyl Groups in the Coordination Sphere of a Ruthenium Complex

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Abstract: Reaction of *o*-styryldiphenylphosphine (*o*-vinylphenyl(diphenyl)phosphine), $o\text{-CH}_2\text{=CHC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$ (SP, I) with $\text{M}_3(\text{CO})_{12}$ (M = Fe or Ru) in refluxing *n*-octane gives monomeric complexes $\text{M}(\text{CO})_3(\text{SP})$ (M = Fe (II); M = Ru (III)) and $\text{M}(\text{CO})_2(\text{SP})_2$ (M = Fe (IV); M = Ru (V)). II and III are five-coordinate molecules containing bidentate SP; IV and V are five-coordinate, trigonal bipyramidal molecules containing one bidentate SP and one monodentate P-bonded SP. In refluxing *n*-nonane, $\text{Ru}_3(\text{CO})_{12}$ and SP react further to give three complexes (VI–VIII) which are formed *via* V. VI which is isomeric with V, is a bis σ -bonded ruthenacyclopentane complex formed by coupling of the free and coordinated vinyl residues of V, *i.e.*, $\text{Ru}(\text{CO})_2\{o\text{-}(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{CHCH}_2\text{CH}_2\text{CHC}_6\text{H}_4\text{P-}(\text{C}_6\text{H}_5)_2\text{-}o\}$. VII is $\text{Ru}(\text{CO})(\text{SP})_2$ derived from V by replacement of one CO by the free vinyl group, which exists in solution in two isomeric forms having different orientations of the coordinated SP ligands. The final complex VIII is derived from VII by dehydrogenation and coupling of the vinyl residues to give the novel tetradentate ligand bis-1,4-[*o*-(diphenylphosphino)phenyl]-1,3-butadiene, *e.g.*, VIII is $\text{Ru}(\text{CO})\{o\text{-}(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{-}c\text{-CH=CH-}r\text{-CH=CHC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-}o\}$. Complexes V and VI are probably in equilibrium in solution at the temperature of refluxing *n*-nonane, VII being formed from V rather than VI. The structure of VI is analogous to intermediates proposed for the tungsten-catalyzed olefin metathesis reaction and for rhodium-catalyzed rearrangements of strained rings. VIII reacts with 2 equiv of hydrogen chloride or hydrogen bromide to give octahedral ruthenium(II) complexes IX and X containing the novel tridentate ligand bis-1,4-[*o*-(diphenylphosphino)phenyl]-*cis*-2-butene, *e.g.*, the dibromo complex $\text{RuBr}_2(\text{CO})\{o\text{-}(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{CH}_2\text{-}c\text{-CH=CHCH}_2\text{C}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-}o\}$ (X) which can be isolated in two geometrically isomeric forms (Xa and Xb). IX and X are rare examples of stable monoolefin complexes of divalent ruthenium. All complexes reported have been characterized by ir, ^1H nmr, and ^{31}P nmr spectroscopy and in the cases of IV, VI, VIII, and Xa by single-crystal X-ray diffraction analysis. A mechanism involving oxidative addition of vinyl groups to zerovalent ruthenium is suggested for the dehydrogenation reaction.

There has been considerable recent interest in transition metal complexes of unsaturated tertiary phosphines and arsines, both from the point of view of stabilizing metal-olefin coordination and of studying the reactivity of olefins which are coordinated to or in the vicinity of transition metal atoms. Bidentate group V donors containing the *o*-vinylphenyl, *o*-propenylphenyl, or *o*-allylphenyl functions are especially versatile ligands which have been used to form chelate monoolefin complexes with the zerovalent group VI metals,^{1,2} vanadium(0),³ manganese(I),⁴ rhenium(I),⁴ iron(0),⁵ ruthenium(0),⁵ ruthenium(II),⁶ rhodium(I),^{7,8} iridium(I),⁹ palladium(II),¹⁰ platinum(II),¹⁰ copper(I),¹¹ and silver(I).¹¹ While it is frequently not possible to isolate stable intermediates in metal-catalyzed olefin reactions, stable, chelate σ -bonded metalocycles are formed by

electrophilic attack on platinum(II),¹² gold(I),¹³ rhodium(I),¹⁴ iron(0),¹⁵ and ruthenium(0)¹⁵ complexes of such ligands, by nucleophilic attack on planar platinum(II) complexes of ligands such as allyldiphenylphosphine,¹⁶ and by the addition of transition metal hydrides to the double bonds of the ligands.^{17,18} We now report in detail on the iron(0) and ruthenium(0) complexes of *o*-styryldiphenylphosphine (SP) (I) and show that two molecules of this ligand coordinated to ruthenium undergo coupling of the vinyl residues and dehydrogenation of the resulting alkane.

Results

Reaction of I (SP) (1 mol per g-atom of Fe or Ru) with the trimetal dodecacarbonyls $\text{M}_3(\text{CO})_{12}$ (M = Fe or Ru) in refluxing 80–100° petroleum ether, *n*-heptane, or *n*-octane gives complexes of formula $\text{M}(\text{CO})_3(\text{SP})$ [M = Fe (II) or Ru (III)] as air-stable solids which are very soluble in all organic solvents and which readily

(1) L. V. Interrante, M. A. Bennett, and R. S. Nyholm, *Inorg. Chem.*, **5**, 2212 (1966).

(2) M. A. Bennett, R. S. Nyholm, and J. D. Saxby, *J. Organometal. Chem.*, **10**, 301 (1967).

(3) L. V. Interrante and G. V. Nelson, *ibid.*, **25**, 153 (1970).

(4) L. V. Interrante and G. V. Nelson, *Inorg. Chem.*, **7**, 2059 (1968).

(5) M. A. Bennett, G. B. Robertson, I. B. Tomkins, and P. O. Whimp, *Chem. Commun.*, 341 (1971).

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

(7) M. A. Bennett and E. J. Hann, *J. Organometal. Chem.*, **29**, C15 (1971).

(8) P. R. Brookes, *ibid.*, **42**, 459 (1972); **43**, 415 (1972).

(9) E. J. Hann, Ph.D. Thesis, Australian National University, 1972.

(10) M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *Inorg. Chem.*, **7**, 556 (1968).

(11) M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *ibid.*, **7**, 552 (1968).

(12) (a) M. A. Bennett, G. J. Erskine, and R. S. Nyholm, *J. Chem. Soc. A*, 1260 (1967); (b) M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *J. Organometal. Chem.*, **26**, 293 (1971).

(13) M. A. Bennett, Kathleen Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson, and A. D. C. Towl, *J. Amer. Chem. Soc.*, **93**, 4591 (1971).

(14) M. A. Bennett, S. J. Gruber, E. J. Hann, and R. S. Nyholm, *J. Organometal. Chem.*, **29**, C12 (1971).

(15) M. A. Bennett, G. B. Robertson, I. B. Tomkins, and P. O. Whimp, *ibid.*, **32**, C19 (1971).

(16) W. Hewertson and I. C. Taylor, *Chem. Commun.*, 428 (1970).

(17) (a) P. R. Brookes and R. S. Nyholm, *ibid.*, 169 (1970); (b) P. R. Brookes, *J. Organometal. Chem.*, **47**, 179 (1973).

(18) M. A. Bennett and R. Watt, *Chem. Commun.*, 94 (1971).

Table I. Analytical, Melting Point, and Ir Data^a

Complex	Mp, °C	% C		% H		% Cl/Br		% P		Mol wt		Medium	Other bands (cm ⁻¹) (Nujol mulls)
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
II	45-47	64.3	65.3	4.0	3.9			7.2	7.4 ^b			Cyclo-hexane	1250 w, ^g 895 m ^h
III	63-64	58.3	60.9	3.6	4.3			6.6	6.9			<i>n</i> -Octane	1245 w, ^g 895 m ^h
IV	>175 dec	73.2	72.8	4.9	4.9			9.0	9.0	688	680 ^c	Cyclo-hexane	1625 vw, ⁱ 1248 m, ^g 990 m, ^j 918 m, ^k 895 w ^h
V	>175 dec	68.8	68.7	4.7	4.7			8.4	8.0			Cyclo-hexane	1625 vw, ⁱ 1245 w, ^g 988 m, ^j 915 m, ^k 890 w ^h
VI	92-94	68.8	68.9	4.7	4.7			8.4	7.9	734	716 ^d	Nujol	
VII	>215 dec	69.8	69.7	4.9	5.2			8.8	8.3	706	726 ^d	Nonane Nujol	
VIII	>250 dec	70.0	69.1	4.6	4.8			8.8	8.4			Nonane Nujol	1245 w, ^g 878 s ^h
IX(ii)	nm	63.4	62.1	4.4	4.8	9.1	10.5 ^e	8.0	7.7	776	783 ^f	Nonane	
X(i)	nm	56.9	55.8	4.0	4.1	18.5	20.9 ^e	7.2	7.2			Nujol	
X(ii)	nm	56.9	56.7	4.0	4.1	18.5	18.6	7.2	7.2	865	868 ^f	Nujol	

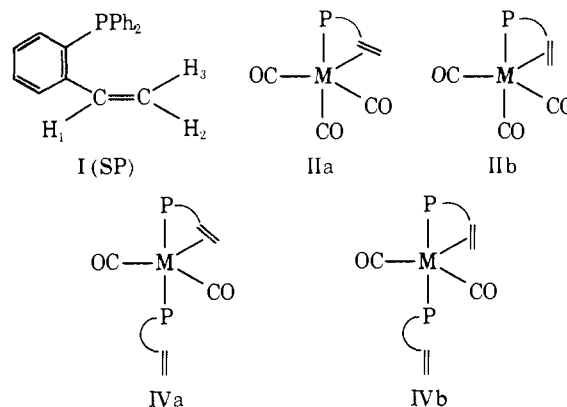
^a Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; nm, not measured. ^b % Fe; calcd, 8.1; found, 8.0. ^c By osmometry in C₆H₆ at 25°. ^d By osmometry in C₆H₆ at 25°. ^e By osmometry in CHCl₃ at 25°. ^f Tentatively assigned to coupled mode involving $\nu(\text{C}=\text{C}) + \delta(\text{CH}_2)$. ^g Tentatively assigned to out of plane $\delta(\text{CH})$ mode of free vinyl group. ^h $\nu(\text{C}=\text{C})$ of free vinyl group. ⁱ Out of plane $\delta(\text{CH})$ mode of free vinyl group. ^j Out of plane $\delta(\text{CH}_2)$ mode of free vinyl group. ^k Out of plane $\delta(\text{CH}_2)$ mode of free vinyl group.

form oils or glasses. They show three strong terminal $\nu(\text{CO})$ bands in their ir spectra (Table I), in addition to bands at ~ 1245 and ~ 895 cm⁻¹ which are characteristic of the coordinated vinyl group; these are tentatively assigned to $\delta(\text{CH}_2) + \nu(\text{C}=\text{C})$ (coupled) and $\delta(\text{CH})$ modes, respectively, by analogy with recent studies on platinum(II) olefin complexes.^{19,20} The mass spectra of the complexes show parent ion peaks and fragment ion peaks due to $\text{M}(\text{CO})_n(\text{SP})$ ($n = 2, 1, 0$). The ¹H nmr spectra of II and III show three groups of resonances due to the vinyl protons which are shifted well upfield from those of the free ligand (Table II). This feature and the magnitudes of the ³¹P coupling to all the olefinic protons provide strong evidence for coordination of the double bond. Complexes II and III are probably trigonal bipyramidal (IIa) with the olefin occupying an equatorial position, as is found in other monoolefin iron carbonyl complexes (see below).

If the reactions between SP and $\text{M}_3(\text{CO})_{12}$ are carried out under the same conditions as above using 2 mol of ligand per g-atom of metal, the main products are yellow dicarbonyls $\text{M}(\text{CO})_2(\text{SP})_2$ ($\text{M} = \text{Fe}$ (IV) or Ru (V)). To obtain good yields of the iron compound IV, we have found it essential to use freshly prepared $\text{Fe}_3(\text{CO})_{12}$. Both compounds are air-stable and soluble in all organic solvents, and they show two strong terminal $\nu(\text{CO})$ bands in their ir spectra (Table I).

Although the spectroscopic and X-ray evidence discussed below leaves no doubt about the formulation of IV and V as dicarbonyls, the mass spectra of these complexes are somewhat misleading at first sight. Both complexes show weak parent ion peaks and strong peaks due to $\text{M}(\text{SP})_2^+$, but in addition a series of peaks arising from $\text{M}(\text{CO})_n(\text{SP})$ ($n = 3, 2, 1, \text{ or } 0$) is observed; these presumably arise by disproportionation and CO migration in the mass spectrometer.

In addition to bands in the ir at ~ 1240 and ~ 895 cm⁻¹ typical of the coordinated vinyl group, there are bands at ~ 990 and ~ 920 cm⁻¹ which can be assigned to $\delta(\text{CH}_2)$ and $\delta(\text{CH})$ modes of a free vinyl group, and there is also a weak band at 1625 cm⁻¹ due to the $\nu(\text{C}=\text{C})$ mode of the latter. The ¹H nmr spectra of IV and V show resonances due to a free and a



coordinated vinyl group in a 1:1 ratio. The chemical shifts of the β -protons of the free vinyl group are very similar to those in SP itself, whereas those of the coordinated vinyl group are shifted well upfield and appear

(19) (a) J. Hiraishi, *Spectrochim. Acta, Part A*, **25**, 749 (1969); (b) J. Hiraishi, D. Finseth, and F. A. Miller, *ibid.*, **25**, 1657 (1969).

(20) D. B. Powell, J. G. V. Scott, and N. Sheppard, *ibid.*, **28**, 327 (1972).

Table II. ^1H Nmr Spectra of Iron and Ruthenium Carbonyl Complexes of $\text{SP}^{\text{a},\text{b}}$

	Chemical shifts			Coupling constants					
	$\delta(\text{H}_1)$	$\delta(\text{H}_2)$	$\delta(\text{H}_3)$	$ J_{13} $	$ J_{12} $	$ J_{23} $	$ J_{\text{P-H}_1} $	$ J_{\text{P-H}_2} $	$ J_{\text{P-H}_3} $
SP	<i>c</i>	4.99 (dd)	5.45 (dt)	17.5	11.0	1.3	Nil	1.1	Nil
$\text{Fe}(\text{CO})_3(\text{SP})$ (II)	4.0 (8 lines)	2.73 (7 lines)	1.94 (dt)	9.8	8.5	2.3	4.6	5.6	9.4
$\text{Ru}(\text{CO})_3(\text{SP})$ (IV)	3.96 (6 lines)	2.45 (7 lines)	1.62 (dt)	9.0	8.5	3.0	3.5	5.0	8.0
coordinated	2.98 (m)	2.3 (m)	2.3 (m)	<i>d</i>	<i>d</i>	<i>d</i>	4.0 (P ₁)	<i>d</i>	<i>d</i>
$\text{Fe}(\text{CO})_2(\text{SP})_2$ (III)							4.0 (P ₂)		
free	<i>c</i>	5.10 (d)	5.50 (d)	17.0	10.0	~ 0	Unknown	Nil	Nil
coordinated	2.84 (m)	1.90 (m)	1.90 (m)	<i>d</i>	<i>d</i>	<i>d</i>	4.0 (P ₁)	<i>d</i>	<i>d</i>
$\text{Ru}(\text{CO})_2(\text{SP})_2$ (V)							4.0 (P ₂)		
free	<i>c</i>	5.10 (d)	5.50 (d)	17.0	11.0	~ 0	Unknown	Nil	Nil
$\text{Ru}(\text{CO})(\text{SP})_2$ (VII)	3.74 (m)(A)	2.99 (m)(B)	2.41 (m)(C)	8.2	8.2	1.4	<i>f</i>	<i>f</i>	<i>f</i>
(2 isomers, 3	3.57 (m)(D)	2.33 (m)(E)	2.00 (m)(F)	9.5	8.5	1.2	<i>f</i>	<i>f</i>	<i>f</i>
different vinyl	3.44 (m)(G)	2.19 (m)(H)	2.02 (m)(I)	8.6	8.1	1.4	<i>f</i>	<i>f</i>	<i>f</i>
groups) ^c									

^a Measured in C_6D_6 except where stated otherwise, δ in ppm downfield of TMS, J in Hz; and protons and phosphorus atoms numbered as in I. ^b Abbreviations: m, multiplet; d, doublet; dd, doublet of doublets; dt, 1:2:1 doublet of triplets. ^c Obscured by aromatic resonances. ^d Spectrum too complex to obtain all coupling constants; $1/2(|J_{12}| + |J_{13}|) = 8$. ^e Measured in $\text{C}_6\text{D}_5\text{Br}$ with ^{31}P decoupling; capital letters refer to labeling of resonances in Figure 1. ^f Spectrum too complex to obtain $J_{\text{P-H}}$.

as complex multiplets, presumably because they are coupled to both phosphorus nuclei. The proton-decoupled ^{31}P nmr spectrum of $\text{Ru}(\text{CO})_2(\text{SP})_2$ (V) consists of an AB quartet ($^2J_{\text{P-P}} = 264$ Hz), the chemical shifts being in the expected range for coordinated tertiary phosphines (Table III). The magnitude of $^2J_{\text{P-P}}$ sug-

Table III. ^{31}P Nmr Data^a

Complex	Multiplicity	$\delta_{\text{P}}^{\text{b}}$	$^2J_{\text{P-P}}^{\text{c}}$
V	AB quartet	57.6, 49.4	264
VI	Singlet	64.1	
VII(i)	Singlet	61.2	
VII(ii)	AB quartet	63.9, 47.2	312
VIII	2 singlets	66.2, 58.8	<6
X(i)	Singlet	41.1	
X(ii)	Singlet	16.2	

^a Measured in CH_2Cl_2 . ^b In ppm from 85% H_3PO_4 external reference, positive shift being to low field side. P_A is taken to be at lower field than P_B by convention, accuracy ± 0.3 ppm. ^c In Hz, accuracy ± 5 Hz.

gests that the phosphorus atoms are mutually trans, in agreement with the result of a single-crystal X-ray study⁶ of the isomorphous iron compound IV which confirms the presence of a free and a coordinated vinyl group and shows that the two phosphorus atoms occupy the axial positions of an approximate trigonal bipyramid (IVa). The two carbonyl groups and the coordinated vinyl group occupy equatorial positions, the $\text{C}=\text{C}$ bond subtending an angle of 6° with the equatorial plane. The geometry of the coordinated olefin is very similar to that found in the $\text{Fe}(\text{CO})_4$ complexes of ethylene,²¹ acrylonitrile,²² and fumaric acid.²³ Molecular models indicate that there are two possible limiting configurations for the vinyl group of coordinated SP in complexes such as II–V, the double bond being oriented either approximately in or approximately at right angles to the equatorial plane (IIa, IVa and IIb, IVb, respectively). The appearance of six or seven $\nu(\text{CO})$ bands in the ir spectra of $\text{M}(\text{CO})_4$ -

(SP) ($\text{M} = \text{Mo}$ or W) has been taken²⁴ to suggest that a mixture of isomers having different orientations of the coordinated vinyl group is present in solutions of these complexes, but there was no comparable ir evidence for isomerism in complexes II–V.

The ^1H nmr data for complexes II–V can be compared with those of other metal chelate complexes of SP. For complexes such as $\text{M}(\text{CO})_4(\text{SP})$ ($\text{M} = \text{Cr}$, Mo , or W),^{2,24} $\text{RhCl}(\text{SP})_2$,^{7,8} $\text{Pt}(\text{CH}_3)_2(\text{SP})$,²⁵ $\text{PtCl}(\text{CH}_3)(\text{SP})$,²⁵ or $\text{RuX}_2(\text{SP})_2$ ($\text{X} = \text{Cl}$ or Br),⁶ the β -vinyl proton resonances have been assigned on the basis that the trans-coupling J_{13} is greater than the cis-coupling J_{12} , as is the case for SP itself; this means that, in most of these complexes, the resonance due to H_3 appears at higher field than that due to H_2 , whereas the reverse is true for the free ligand. However, for complexes II–V, J_{13} and J_{12} are almost equal numerically, and we have therefore arbitrarily assigned the resonance at highest field to H_3 (Table II); this leads to J_{13} being slightly greater than J_{12} .

Surprisingly the complexes $\text{M}(\text{CO})_3(\text{SP})$ (II and III) are not the precursors to $\text{M}(\text{CO})_2(\text{SP})_2$ (IV and V), even though the latter are formally derived from the former by replacement of an axial CO by P-bonded monodentate SP. Thus, II is recovered unchanged on heating with one molar equivalent of SP in *n*-heptane, and it also fails to react with triphenylphosphine or trimethylphosphite. We suggest that the common precursors to II–V are the monodentate P-bonded tetracarbonyls $\text{M}(\text{CO})_4(\text{SP})$ ($\text{M} = \text{Fe}$ or Ru) which can either lose CO to form the chelate complexes II and III or, in the presence of an excess of SP, can form the trans disubstituted, monodentate, P-bonded complexes $\text{M}(\text{CO})_3(\text{SP})_2$; these can then lose CO to give IV and V. The fact that the complexes $\text{Fe}(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_5)_3\}$ and *trans*- $\text{Fe}(\text{CO})_3\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ can be isolated from the reaction of $\text{Fe}_3(\text{CO})_{12}$ with triphenylphosphine²⁶ lends support to this proposal.

Two new complexes are obtained from the reaction of an excess of SP with $\text{Ru}_3(\text{CO})_{12}$ in refluxing *n*-nonane for 1 hr. The first complex, VI, which remains in

(21) M. I. Davis and C. S. Speed, *J. Organometal. Chem.*, **21**, 401 (1970).

(22) A. R. Luxmoore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962).

(23) C. Pedone and A. Sirigu, *ibid.*, **23**, 759 (1967); *Inorg. Chem.*, **7**, 2614 (1968).

(24) M. A. Bennett and I. B. Tomkins, *J. Organometal. Chem.*, **51**, 283 (1973).

(25) M. A. Bennett, R. Bramley, and I. B. Tomkins, *J. Chem. Soc., Dalton Trans.*, 166 (1973).

(26) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

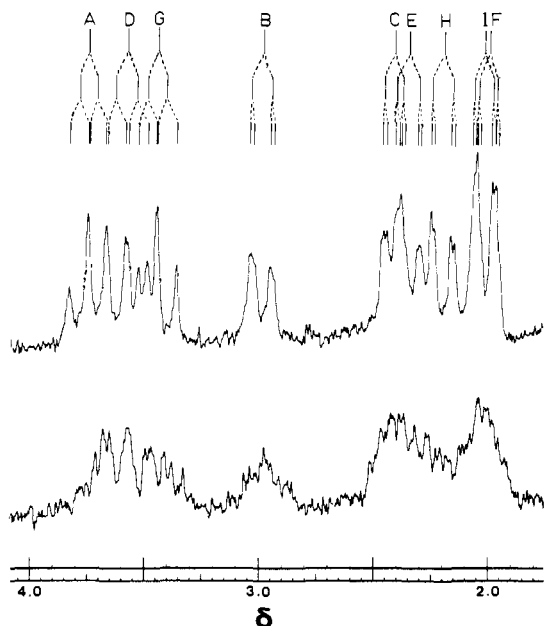


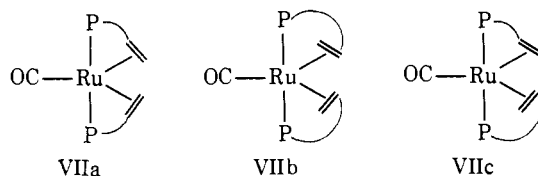
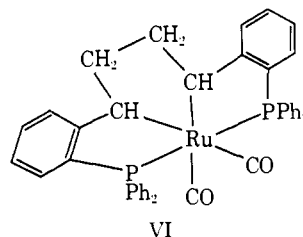
Figure 1. Proton nmr spectrum of $\text{Ru}(\text{CO})(\text{SP})_2$ (VII) in $\text{C}_6\text{D}_5\text{Br}$ at 100 MHz: top trace is ^{31}P -decoupled spectrum. (A, B, C), (D, E, F), and (G, H, I) denote chemical shifts of the mutually coupled vinyl protons of isomers VII(i) and VII(ii) (see text).

solution, is isomeric with complex V and has a parent ion at m/e 734 (^{102}Ru) in its mass spectrum; ions arising from the successive loss of two carbonyl groups are also observed. The appearance of two strong $\nu(\text{CO})$ bands in the ir spectrum also indicates that VI is a dicarbonyl. The complex has been shown by single-crystal X-ray diffraction analysis²⁷ to be an octahedral σ -bonded dicarbonyl complex of ruthenium(II) containing a puckered ruthenacyclopentane ring formed by the coupling of two vinyl residues at the β -carbon atoms (structure VI). The proton-decoupled ^{31}P nmr spectrum of VI shows a singlet, as expected for two equivalent mutually trans phosphorus atoms. We would have expected an AA'BB'CC' spectrum for the protons in the butane chain, but in fact the methylene protons are fortuitously equivalent and the resulting AA'BB'-B''B''' spectrum consists (after ^{31}P decoupling) of a quintet for the methine protons and a triplet for the methylene protons. The observed splitting of 2.3 Hz appears reasonable for the average of two gauche vicinal (3J) and two long-range (4J) couplings in the aliphatic chain. Nmr data alone do not unambiguously exclude the alternative formulation of VI as a ruthenium(0) olefin complex of the tridentate ligand bis-1,4-[*o*-(diphenylphosphino)phenyl]-*cis*-2-butene, $\text{Ru}(\text{CO})_2\{\text{o}-(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CHCH}_2\text{C}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{o}\}$, although if the long range coupling (5J) between the methylene protons were small (as is true for ruthenium(II) complexes containing this ligand (see below)), the olefinic protons would have appeared as a triplet rather than as the quintet observed.

The second complex, VII, is insoluble in *n*-nonane and precipitates from the reaction mixture. The pale yellow compound has the molecular formula $\text{Ru}(\text{CO})(\text{SP})_2$ and it shows only one $\nu(\text{CO})$ band, both in the solid state and in dichloromethane. The presence of coordinated SP is indicated by characteristic bands at

(27) P. O. Whimp, personal communication; details will be published elsewhere.

1245 and 878 cm^{-1} in the ir spectrum (see above), but there are no bands assignable to a free vinyl group. The mass spectrum shows a parent ion at m/e 706 (^{102}Ru). The ^1H nmr spectrum of VII is very complex but is simplified by ^{31}P decoupling to give, in addition to signals due to aromatic protons, six "doublets" and three "triplets" (Figure 1). $^1\text{H}-\{^1\text{H}\}$ decoupling experiments show that there are three sets of mutually coupled protons, the chemical shifts of which are denoted by (A, B, C), (D, E, F), and (G, H, I) in Figure 1. Each set gives a spectrum consisting of one "triplet" and two "doublets," and the chemical shifts and coupling constants of each set are similar both to those of the other two sets and to those of $\text{Ru}(\text{CO})_3(\text{SP})_2$ (III) (Table II). Thus, the molecule $\text{Ru}(\text{CO})(\text{SP})_2$

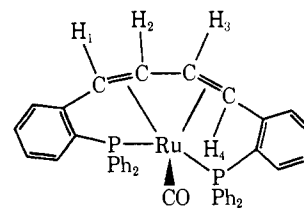


apparently contains *three* different coordinated vinyl groups. The only way to account for this surprising observation is to assume that $\text{Ru}(\text{CO})(\text{SP})_2$ contains two chelate SP ligands in a five-coordinate structure (probably trigonal bipyramidal) and to postulate the presence in solution of two isomers, of which one (VII(i)) has equivalent vinyl groups and the other (VII(ii)) has inequivalent vinyl groups. To account for the observed 1:1:1 ratio of vinyl resonances, one must assume that VII(i) and VII(ii) are present in a ratio of approximately 1:2. In good agreement with these seemingly *ad hoc* assumptions, the proton-decoupled ^{31}P nmr spectrum shows a singlet and an AB quartet which we assign to VII(i) and VII(ii), respectively. The former thus has equivalent vinyl groups and equivalent phosphorus atoms, whereas the latter has inequivalent vinyl groups and inequivalent phosphorus atoms. The magnitude of $^2J_{\text{P-P}}$ (312 Hz) suggests that VII(ii) has trans phosphorus atoms, and we assume the same to be true for VII(i).

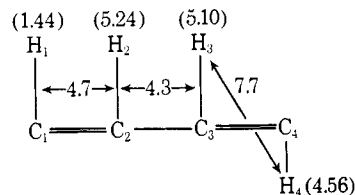
Preliminary studies indicate that the isomers interconvert with increasing temperature. At $\sim 70^\circ$ some of the ^1H nmr signals begin to broaden and at 142° they have coalesced to give a triplet and two doublets as expected for a coordinated vinyl group, although at this temperature the signals are still broad. Although there is partial irreversible decomposition (see below), variable temperature ^{31}P nmr studies should throw light on the nature of the isomers and the mechanism of their interconversion. We note at this stage that if both vinyl groups are in the equatorial plane, there are three possible geometric isomers which arise from different orientations of the vinyl groups with respect to each other, *i.e.*, head-to-head (VIIa), tail-to-tail (VIIb), and head-to-tail (VIIc). VIIa and VIIb have equivalent

vinyl groups and equivalent phosphorus atoms, while VIIc has inequivalent vinyl groups and inequivalent phosphorus atoms. If one or both of the vinyl groups are allowed to be perpendicular to the coordination plane, a further seven isomers arise, two of which have inequivalent vinyl groups. It seems unlikely that *both* vinyl groups will be in this orientation, which has not so far been observed for trigonal bipyramidal olefin complexes, but VII(ii) could well have one vinyl group in the equatorial plane and the other perpendicular to it. On the other hand, the $\nu(\text{CO})$ frequencies of the two isomers in cyclohexane are identical within the limits of resolution ($\sim 2 \text{ cm}^{-1}$), whereas in $\text{M}(\text{CO})_4(\text{SP})$ ($\text{M} = \text{Mo}$ or W) the frequencies of the two isomers are measurably different.²⁴ On the basis of this admittedly negative evidence, we suggest that VII(ii) has the unsymmetrical structure VIIc and that VII(i) has either of the symmetrical structures VIIa or VIIb; in all three structures the vinyl groups are in the equatorial plane.

If $\text{Ru}_3(\text{CO})_{12}$ and excess SP are heated in *n*-nonane for several hours, both VI and VII, which are initially formed, are converted into a deep yellow, monomeric complex, VIII, which has been identified by analysis, nmr spectroscopy, and single-crystal X-ray diffraction analysis²⁷ as a monocarbonylruthenium(0) derivative of the tetradentate cisoid diene ligand bis-1,4-[*o*-(diphenylphosphino)phenyl]-1,3-butadiene. The fate of the hydrogen lost in this process has not been determined. The ir spectrum of VIII shows only one $\nu(\text{CO})$ band (Table I), the mass spectrum shows a parent ion peak (M^+) at m/e 704 (^{102}Ru), together with a peak due to ($\text{M}^+ - \text{CO}$), and the ^1H nmr spectrum shows, in addition to aromatic resonances, four multiplets of equal intensity which can readily be assigned to the coordinated diene protons. According to the X-ray study, the geometry and bond lengths of the coordinated diene are similar to those found in $\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_6)$ ²⁸ and in other acyclic diene iron tricarbonyls.^{29,30} The (*o*-diphenylphosphino)phenyl substituents are not equivalent, but occupy syn and anti positions respectively with respect to the two central diene protons H_3 and H_2 , the P-Ru-P angle being 108° . The essentially cis disposition of the two phosphorus atoms probably accounts for the very small value of $^2J_{\text{P-P}}$ (Table III). In the ^1H nmr spectrum of VIII the highest field resonance at δ 1.44 must be assigned to one of the terminal protons on the basis of data for acyclic diene iron tricarbonyls,³¹ but it is not obvious whether it corresponds to H_1 or H_4 , which are *exo* and *endo*, respectively, with respect to the metal atom. It is interesting that this resonance also shows an abnormally large coupling (13 Hz) with one of the phosphorus atoms. Depending on the choice for the highest field resonance, $^1\text{H}-\{^1\text{H}\}$ decoupling establishes the two possible assignments VIIa and VIIb for the rest of the spectrum. Both assignments have a terminal proton (H_4 in VIIa, H_1 in VIIb) at anomalously low field in comparison with the values for terminal protons in diene iron tricarbonyls, and in VIIb the magnitude of the *trans* coupling J_{34} is smaller than that of the *cis* coupling, which would be most un-



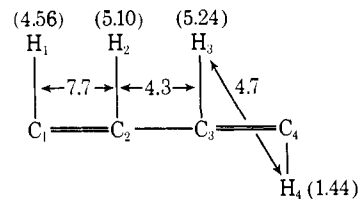
VIII



$$J_{13} = 0.9; J_{24} = 1.0; J_{\text{P-H}_1} = 4.5, 13.0;$$

$$J_{\text{P-H}_2} = 0, 3.8; J_{\text{P-H}_3} = 0, 1.8; J_{\text{P-H}_4} = 2.0, 2.5$$

VIIa



$$J_{13} = 1.0; J_{24} = 0.9; J_{\text{P-H}_1} = 2.0, 2.5;$$

$$J_{\text{P-H}_2} = 0, 1.8; J_{\text{P-H}_3} = 0, 3.8; J_{\text{P-H}_4} = 4.5, 13.0$$

VIIIb

Chemical shifts (δ) are in ppm downfield of internal TMS, coupling constants (J) are in Hz.

usual for an olefinic system. For this reason we favor assignment VIIa and suggest that H_4 may be in the deshielding zone of the Ru-CO moiety. This is supported by an examination of the molecular structure, which also shows that C_1 , to which the shielded proton H_1 is attached, is almost *trans* to the phosphorus atom of the diphenylphosphino substituent on C_4 (the angle at the metal atom, P-Ru- C_1 is 161°). This feature might account for the large ^3P coupling noted above.

In contrast with diene iron tricarbonyls, which add one molecule of hydrogen chloride to give π -allylic complexes of the type $\text{FeCl}(\pi\text{-allyl})(\text{CO})_3$,³² complex VIII undergoes addition of two molecules of HCl or HBr to give crystalline, monomeric ruthenium(II) complexes containing the tridentate olefinic ligand bis-1,4-[*o*-(diphenylphosphino)phenyl]-*cis*-2-butene, $\text{RuX}_2(\text{CO})\{o\text{-(C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CHCH}_2\text{C}_6\text{H}_4\text{P(C}_6\text{H}_5)_2\text{-}o\}$ ($\text{X} = \text{Cl}$ (IX) or Br (X)). Both compounds exist in isomeric forms. The orange crystalline bromo complex X(i) initially isolated, which has $\nu(\text{CO})$ at 2010 cm^{-1} (Nujol), isomerizes slowly in dichloromethane or more rapidly on successive recrystallizations from dichloromethane-methanol, to the more stable orange isomer X(ii) which has $\nu(\text{CO})$ at 1989 cm^{-1} (Nujol). The HCl reaction gives as the main product a colorless crystalline complex IX(ii) with $\nu(\text{CO})$ 1990 cm^{-1} (Nujol), but small amounts of the less stable isomer IX(i) ($\nu(\text{CO})$ 2015 cm^{-1}) can be detected. The ^3P -decoupled ^1H nmr spectra of X(i) and X(ii) (Figure 2) are of the ABX type with couplings of approximately 18, 10, and 0 Hz (Table IV). The

(28) O. S. Mills and G. Robinson, *Acta Crystallogr.*, **16**, 758 (1963).

(29) R. Mason and G. B. Robertson, *J. Chem. Soc. A*, 1229 (1970).

(30) R. Eiss, *Inorg. Chem.*, **9**, 1650 (1970).

(31) G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964).

(32) (a) F. J. Impastato and K. G. Ihrman, *J. Amer. Chem. Soc.*, **83**, 3726 (1961); (b) G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind. (London)*, 836 (1964); (c) T. H. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, **93**, 5296 (1971).

Table IV. ^1H Nmr Data for Ruthenium(II) Complexes of Bis-1,4-[*o*-(diphenylphosphino)phenyl]-*cis*-2-butene^{a,b}

		IX(ii)	X(ii)	X(i)
Chemical shifts (δ)	H _A	4.36	4.38	3.68
	H _B	3.49	3.65	3.36
	H _X	3.30	3.29	6.25
	Aromatic	7.1–7.6 (24 H) 8.0–8.2 (4 H)	6.9–7.6 (24 H) 7.9–8.2 (4 H)	6.8–7.6 (28 H)
Coupling constants (^1H - ^1H) ^c	J _{AB}	-18.0	-18.2	-17.8
	J _{AX}	9.5	9.9	0.5
	J _{BX}	0.5	0.5	9.5
	J _{XX'}	6.8	7.0	8.8
Coupling constants (^1H - ^{31}P) ^d	J _{AP}	~0	~0	1.5
	J _{BP}	2.5	2.1	0
	J _{XP}	3.8	3.9	1.2

^a Measured in CD₂Cl₂ solution. Chemical shifts (δ) are in ppm downfield of internal TMS, coupling constants (J) are in Hz. ^b Arbitrarily labeled butene chain -CH_AH_B-CH_X=CH_{X'}-CH_{A'}H_{B'}-, H_A being downfield of H_B. ^c Estimated errors: J_{AB}, 0.2; J_{AX}, 0.3; J_{BX}, 0.5; J_{XX'}, 1.0. ^d Estimated error of 0.5 Hz in all values.

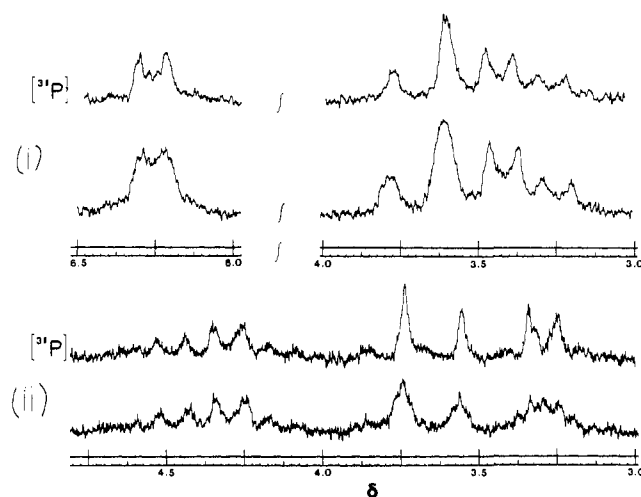
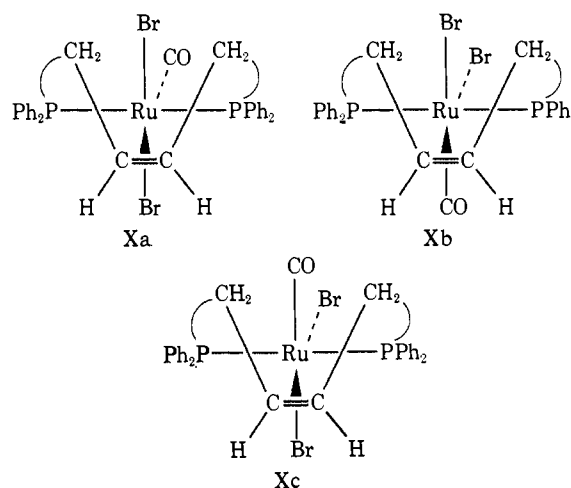


Figure 2. Proton nmr spectra of isomers of RuBr₂(CO){C₆H₅}-PC₆H₄CH₂CH=CHCH₂C₆H₄P(C₆H₅)₂, X(i) and X(ii), in CD₂Cl₂ at 100 MHz. Top trace in each case is ^{31}P -decoupled spectrum.

18-Hz coupling has the magnitude expected for a geminal coupling in a CH₂ group attached to one or more unsaturated carbon atoms, *cf.* C₆H₅CH₂CN, $J_{\text{gem}} = 18 \text{ Hz}$,³³ while the other two values are in the range expected for vicinal couplings. The spin system of the 2-butene fragment is in fact AA'BB'XX', and this is manifested as fine structure in the XX' (olefinic) part of the spectrum. Computer analysis of the six spin system, assuming negligible coupling between the two methylene groups, show that J_{XX'} is slightly smaller than the larger of the two vicinal couplings, so that the system approximates to ABX. The magnitude of J_{XX'} (7–9 Hz) is approximately equal to the *cis* couplings observed for SP in its ruthenium(II) complexes (8–10 Hz) and is considerably smaller than the corresponding *trans* couplings (12–14 Hz),⁶ so that structures for IX(ii), X(i), and X(ii) containing the isomeric *trans*-2-butene ligand can be eliminated. A single-crystal X-ray analysis²⁷ of X(ii) has confirmed the conclusions derived from nmr data, the stereochemistry of the complex being as shown in Xa, with Br *trans* to Br and CO *trans* to the olefin. The marked differences in $\nu(\text{CO})$ (~20 cm⁻¹) and in chemical shifts (~3 ppm) of the coordinated olefinic protons between X(i) and X(ii) suggest that X(i) is either of the geometric isomers Xb or Xc. The

(33) A. A. Bothner-by, *Advan. Magn. Resonance*, **1**, 195 (1965).



structures of the chloro compounds IX(i) and IX(ii) are undoubtedly similar to those of X(i) and X(ii) although at present we have been unable to measure the ^1H nmr spectrum of IX(i) owing to the very small amount available.

Discussion

Although Fe(CO)₄ complexes of olefins such as ethylene, propene, and styrene are known,³⁴ they are air-sensitive and thermally unstable; more stable complexes are formed by olefins bearing electron-withdrawing substituents. No analogous ruthenium complexes were known at the commencement of our work, but recently the ethylene complexes Ru(CO)₂(C₂H₄){P(C₆H₅)₃}₂³⁵ and Ru(C₂H₄){P(C₆H₅)₃}₃,³⁶ and a styrene complex Ru(C₆H₅CH=CH₂){P(C₆H₅)₃}₃³⁶ have been reported. The stabilizing effect of SP on metal olefin coordination in both group VIII and group VI carbonyl complexes may be a consequence of two factors: the presence of the phosphorus donor, which should favor metal-olefin back-bonding, and, probably more important, the presence of the olefin in a chelate group which should reduce the tendency toward olefin dissociation. This chelate effect also stabilizes the metal-phosphorus bond, as is shown by comparison of the

(34) (a) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **46**, 1588 (1963); (b) E. Koerner von Gustorf, M. C. Henry, and C. Di Pietro, *Z. Naturforsch. B*, **21**, 42 (1966).

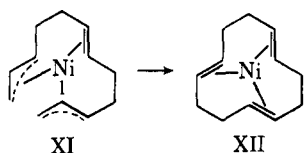
(35) B. E. Cavit, K. R. Grundy, and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 60 (1972).

(36) S. Komiya, A. Yamamoto, and S. Ikeda, *J. Organometal. Chem.*, **42**, C65 (1972).

Fe-P bond lengths of monodentate and bidentate SP in $\text{Fe}(\text{CO})_2(\text{SP})_2$ (2.234 (3) and 2.207 (3) Å, respectively).⁵ We have noted elsewhere¹⁵ that, whereas $\text{Fe}(\text{CO})_4$ -olefin complexes are immediately decomposed by hydrogen halides to give the corresponding alkane, probably *via* intermediate iron σ -alkyls, the $\text{M}(\text{CO})_3(\text{SP})$ complexes react with hydrogen halides to give isolable chelate iron(II) and ruthenium(II) σ -alkyls.

On heating $\text{Ru}(\text{CO})_2(\text{SP})_2$ (V) in *n*-nonane, complexes VI and VII are formed after 1 hr, and formation of VII is complete after ~ 8 hr, as shown by ir monitoring of the reaction at various times. V is therefore the precursor to VI and VII in the $\text{Ru}_3(\text{CO})_{12}$ -SP reaction. If the σ -bonded complex VI is heated in *n*-nonane, its $\nu(\text{CO})$ bands at 1995 and 1945 cm^{-1} decrease in intensity and the band at 1942 cm^{-1} due to VII increases in intensity, over a period of 10–12 hr, after which time the $\nu(\text{CO})$ absorption of VIII at 1924 cm^{-1} begins to appear. Dehydrogenation of VII to form VIII is complete after another 8 hr. Clearly the formation of VII from VI is considerably slower than from V and because of the longer reaction time decomposition is more marked. These qualitative observations suggest that the $\text{Ru}(\text{CO})_2(\text{SP})_2$ (VII) formed in the $\text{Ru}_3(\text{CO})_{12}$ -SP reaction comes from $\text{Ru}(\text{CO})_2(\text{SP})_2$ (V) by direct intramolecular replacement of CO by the uncoordinated vinyl group, and not *via* VI. Presumably a small amount of V is in equilibrium with VI at the temperature of refluxing nonane. Uv irradiation of V in tetrahydrofuran gives VII in low yield as the only isolable organometallic product, but heating or irradiation of $\text{Fe}(\text{CO})_2(\text{SP})_2$ (IV) leads only to decomposition and no iron analogs of VI, VII, or VIII can be isolated by this method. We know of no previous example in which two olefinic groups (one or both coordinated) interact within the coordination sphere of a transition metal complex to give an isomeric complex containing a carbon-carbon bond and two metal-carbon σ bonds.

An analogy in the literature is the interaction of the three butadiene molecules on a nickel atom to give the bis- π -allylic complex XI which rearranges under the influence of heat or of donor ligands to give cyclododecatrienickel (XII).³⁷ It is also worth noting



that metallocyclic species similar to VI have recently been postulated as intermediates in the homogeneously catalyzed tungsten-based olefin metathesis reaction^{38,39} and in the rhodium-catalyzed rearrangements of strained polycyclic rings.^{40,41} In one case involving iridium, a doubly σ -bonded complex has been isolated and identified by single-crystal X-ray analysis.⁴²

The dehydrogenation of VII to the butadiene com-

(37) B. Bogdanović, P. Heimbach, M. Kröner, G. Wilke, E. G. Hoffmann, and J. Brandt, *Justus Liebigs Ann. Chem.*, **727**, 143 (1969).

(38) R. H. Grubbs and T. K. Brunck, *J. Amer. Chem. Soc.*, **94**, 2538 (1972).

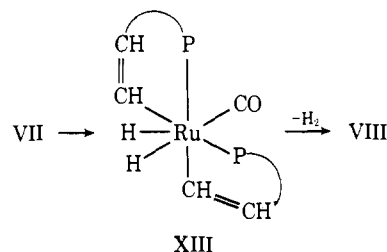
(39) N. Calderon, *Accounts Chem. Res.*, **5**, 127 (1972).

(40) T. J. Katz and S. Cereface, *J. Amer. Chem. Soc.*, **91**, 2405, 6519 (1969).

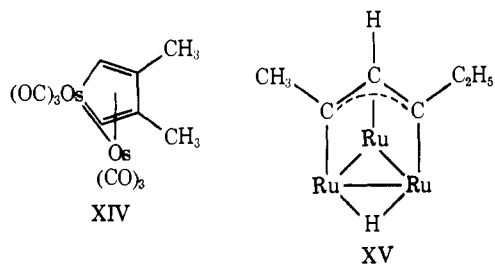
(41) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515 (1970).

(42) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *ibid.*, **95**, 597 (1973).

plex VIII may proceed by oxidative addition of the β -vinyl CH_2 bonds to the metal to give a seven-coordinate dihydrido complex XIII, followed by elimination of



hydrogen and coupling of the *o*-(C_6H_5)₂PC₆H₄CH=CH-residues. A similar mechanism has been proposed for the RhCl_3 -based coupling and dehydrogenation of tri-*o*-tolylphosphine⁴³ and for a variety of intramolecular aromatic metalation reactions.⁴⁴ Dissociation of one or both of the tertiary phosphines during the elimination step in order to preserve sixfold coordination seems unlikely in our case, and we also note that seven-coordinate tetrahydrides of ruthenium(IV), *e.g.*, $\text{RuH}_4\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$, have been isolated.⁴⁵ We know of no previous example of dehydrogenation of an olefinic ligand by a monomeric ruthenium complex, although $\text{Os}_8(\text{CO})_{12}$ is known to react with 2,3-dimethyl-1,3-butadiene to give the binuclear osmacyclopentadiene complex XIV.⁴⁶ More recently, it has been shown that $\text{Ru}_3(\text{CO})_{12}$ abstracts a hydrogen atom from 2,4-hexadiene to give a trinuclear hydrido complex, XV,⁴⁷



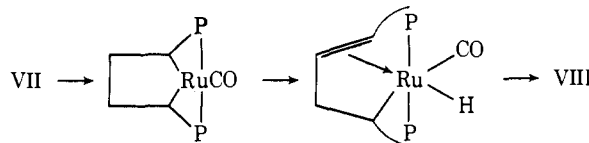
(3 CO groups on each Ru omitted for clarity)

and similar behavior has been noted in the reaction of $\text{Ru}_3(\text{CO})_{12}$ with 1,5,9-cyclododecatriene.⁴⁸ The formation of dihydrides by oxidative addition of olefinic C-H bonds to metal clusters has been observed in the reac-

(43) M. A. Bennett and P. A. Longstaff, *ibid.*, **91**, 6266 (1969).

(44) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

(45) (a) W. H. Knoch, *J. Amer. Chem. Soc.*, **94**, 104 (1972); (b) T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *ibid.*, **92**, 3011 (1970); (c) An alternative mechanism was suggested by a referee. Transformation of VII to VIII could proceed through a coordinatively unsaturated analog of VI, followed by a double β -elimination.



We note that the olefin groups of VII are stable to displacement by CO in refluxing solvents, *e.g.*, toluene or *n*-octane; these conditions should have favored formation of V and VI if this were the correct mechanism.

(46) (a) E. O. Fischer, K. Bittler, and H. P. Fritz, *Z. Naturforsch. B*, **18**, 83 (1963); (b) R. P. Dodge, O. S. Mills, and V. Schomaker, *Proc. Chem. Soc., London*, 380 (1963).

(47) M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J. Chem. Soc., Chem. Commun.*, 545 (1972).

(48) M. I. Bruce, M. A. Cairns, and M. Green, *J. Chem. Soc. Dalton Trans.*, 1293 (1972).

tions of $\text{Os}_3(\text{CO})_{12}$ with ethylene^{49,50} and with SP^{49} and of $\text{Ru}_3(\text{CO})_{12}$ with cyclooctene⁵¹ and with 2,6-bicyclo-[3.2.1]octadiene.⁵² Clearly olefinic C-H bonds oxidatively add to metal carbonyl clusters more readily than to mononuclear metal carbonyls, but in our case the reaction is probably promoted by the presence of two σ -donor phosphorus atoms in place of carbonyl groups. This feature, combined with the stability of the resulting coordinated tridentate olefin, may also help to explain why the butadiene complex VIII adds two molecules of hydrogen halide, whereas $\text{Fe}(\text{CO})_5(\text{C}_4\text{H}_6)$ adds only one. Complexes IX(i), IX(ii), X(i), and X(ii) appear to be the first isolated monoolefin complexes of ruthenium(II), although ethylene⁵³ and acrylonitrile⁵⁴ complexes have been postulated as reaction intermediates.

Experimental Section

Ir spectra were recorded on Perkin-Elmer 457 and 225 spectrophotometers and calibrated with polystyrene. Solid-state spectra were taken either as KBr disks or as Nujol mulls on CsI windows. Solution ir spectra were measured in 1-mm path length cells using CaF_2 and KBr windows. Proton nmr spectra were recorded on a Varian HA-100 spectrometer modified to carry out $\{^1\text{H}-\{^31\text{P}\}$ heteronuclear decoupling. Spectra were obtained in field and/or frequency swept mode using tetramethylsilane as internal lock and reference and were calibrated with a Hewlett-Packard frequency counter. Phosphorus nmr spectra were run on a Jeol C-60-HL spectrometer, modified for $\{^31\text{P}-\{^1\text{H}\}$ heteronuclear decoupling, using frequencies derived from a synthesizer for the ^1H external lock and ^31P observation channels. Spectra were accumulated using a PDP-8I computer. Mass spectra were measured by Mr. K. Goggin on an AEI-MS9 instrument at 70 eV. Melting points were determined on samples sealed in capillaries under nitrogen using a Gallenkamp apparatus and are uncorrected. Analyses and osmometric molecular weight measurements (Model 301A, Mechrolab) were carried out by the 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.

All solvents (AR grade) were dried over molecular sieves (BD-H4A). The trimetal dodecacarbonyls $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ were prepared by literature methods,^{55,56} except that a pressure of 90 atm of carbon monoxide at 90° was used in the $\text{Ru}_3(\text{CO})_{12}$ preparation instead of the stated 10 atm at 65°.

Preparations. Tricarbonyl(*o*-styryldiphenylphosphine)iron(0), $\text{Fe}(\text{CO})_3(\text{SP})$ (II) and Dicarbonylbis(*o*-styryldiphenylphosphine)iron(0), $\text{Fe}(\text{CO})_2(\text{SP})_2$ (IV). A mixture of *o*-styryldiphenylphosphine (0.9 g, 2 mol per g-atom of Fe) and freshly prepared $\text{Fe}_3(\text{CO})_{12}$ (0.25 g) in petroleum ether (40 ml of bp 80–100°) was heated and stirred at 80° for 45 min in a nitrogen atmosphere. After cooling to room temperature, the yellow precipitate was filtered off, washed with three 5-ml portions of hot petroleum ether (80–100°), and dried *in vacuo*. Recrystallization from benzene-*n*-hexane (1:1) under nitrogen gave yellow microcrystals of IV. The filtrate was kept overnight at 0° whereupon a further crop of deep yellow crystals of IV separated. Total yield of IV was 0.72 g (70%).

After removal of the yellow crystals, the supernatant solution was chromatographed on silica gel (100–200 mesh, made up in 80–100° petroleum ether). A yellow band which was eluted with benzene was collected and evaporated to dryness on a rotary evaporator. The residual yellow-brown oil was redissolved in *n*-pentane, solvent was removed, and the oil was heated at 50° (10⁻³ mm) for 10 days. On cooling to room temperature, the product slowly solidified to a

yellow-brown glass from which traces of residual solvent were difficult to remove. Yield of II was 0.13 g (20%).

It was isolated in 75% yield as the sole product from the reaction of "old" $\text{Fe}_3(\text{CO})_{12}$ (0.5 g) and SP (0.9 g, 1 mol per g-atom of Fe). Use of freshly prepared $\text{Fe}_3(\text{CO})_{12}$ in this reaction gave II in 60% yield and IV in 20% yield.

Tricarbonyl(*o*-styryldiphenylphosphine)ruthenium(0), $\text{Ru}(\text{CO})_3(\text{SP})$ (III). A mixture of *o*-styryldiphenylphosphine (0.68 g, 1 mol per g-atom of Ru) and $\text{Ru}_3(\text{CO})_{12}$ (0.5 g) was heated under nitrogen in *n*-octane (40 ml) for 2 hr. The solution initially turned deep reddish purple, then became deep orange. On cooling to room temperature, a small quantity of yellow insoluble material separated out and was removed by filtration. Solvent was removed on the rotary evaporator and the oily residue was redissolved in the minimum volume of hot *n*-octane. On partial evaporation of the solvent, the orange crystalline product III was deposited. The solution was decanted and the procedure was repeated. The product was washed with *n*-pentane at -78° and dried at 50° (10⁻³ mm) for 3 days to give 0.83 g (75%) of III. Traces of solvent and, in some preparations, of $\text{Ru}_3(\text{CO})_{12}$ were still present. After being melted, the complex only slowly resolidified to a glass.

Dicarbonylbis(*o*-styryldiphenylphosphine)ruthenium(0) $\text{Ru}(\text{CO})_2(\text{SP})_2$ (V). A mixture of *o*-styryldiphenylphosphine (1.0 g, 3.5 mol per g-atom of Ru) and $\text{Ru}_3(\text{CO})_{12}$ (0.25 g) in *n*-heptane (50 ml) was stirred and heated under reflux in a nitrogen atmosphere for 1.5 hr. The yellow suspension was filtered while still hot, and the orange-brown insoluble solid was washed with small amounts of hot *n*-heptane. Recrystallization from the minimum volume of cyclohexane-*n*-hexane (1:1) gave yellow microcrystals of V. On storage overnight at 0° the filtrate deposited a second crop of pure V, which was collected by filtration, washed with ice-cold *n*-pentane, and finally dried *in vacuo*. Yield was 0.5 g (60%, based on Ru).

2,5-[Bis(*o*-diphenylphosphino)phenyl](dicarbonylruthena)cyclopentane, $\text{Ru}(\text{CO})_2\{o\text{-}(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{CHCH}_2\text{CH}_2\text{CHC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-}o\}$

(VI) and Carbonylbis(*o*-styryldiphenylphosphine)ruthenium(0), $\text{Ru}(\text{CO})(\text{SP})_2$ (VII). *o*-Styryldiphenylphosphine (0.8 g, 3 mol per g-atom of Ru) and $\text{Ru}_3(\text{CO})_{12}$ (0.2 g) in *n*-nonane (50 ml) were stirred and heated under reflux in a nitrogen atmosphere for 1 hr. The solution was allowed to cool to room temperature and was set aside overnight. The yellow supernatant liquid was carefully decanted and the remaining yellow-brown solid (impure VII) was washed with two 5-ml portions of *n*-nonane. These washings were added to the supernatant solution, which was filtered and evaporated to ~30 ml on the rotary evaporator. The solution was then chromatographed on a silica gel column (100–200 mesh) made up in *n*-heptane, and eluted with *n*-heptane to remove *n*-nonane and unreacted ligand. Benzene-*n*-heptane (1:1) eluted a pale yellow band which was collected and evaporated to dryness under reduced pressure. The residue was recrystallized from dichloromethane-methanol (1:4) at room temperature over a period of 2–3 days. The colorless crystals of VI were washed with methanol and dried *in vacuo* (0.15 g, 22%, based on Ru). ^1H nmr (CD_2Cl_2): δ 7.04–7.80 (m, 28 H, aromatic), 2.92 (m, 2 H, CHCH_2), 1.08 (m, 4 H, CHCH_2), $J_{\text{CHCH}_2} = 2.3$, $J_{\text{P-CH}} = 4.6$, $J_{\text{P-CH}_2} = 1.2$ Hz.

The impure VII from the above reaction was washed with small amounts of acetone to remove the brown color, and the resulting pale yellow solid was dried in a stream of nitrogen. It was then redissolved in the minimum volume of dichloromethane under nitrogen, and the pure, pale yellow crystalline product was obtained by addition of methanol. After washing with methanol and drying *in vacuo*, the yield (based on Ru) was 0.2 g (30%).

Preparation of $\text{Ru}(\text{CO})(\text{SP})_2$ (VII) from $\text{Ru}(\text{CO})_2(\text{SP})_2$ (V). V (0.1 g) in dry tetrahydrofuran (30 ml) under nitrogen was irradiated for 4 hr using a water-cooled medium-pressure mercury lamp (Engelhard Hanovia, 125 W), and solvent was then removed *in vacuo*. Ir spectra of the orange-brown residue (Nujol mull and dichloromethane solution) showed that the only carbonyl-containing organometallic product was VII; there was considerable decomposition.

Carbonylbis-1,4-[*o*-(diphenylphosphino)phenyl]-1,3-butadieneruthenium(0), $\text{Ru}(\text{CO})\{o\text{-}(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{CH}=\text{CHCH}=\text{CHC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-}o\}$ (VIII). Complex VII (0.2 g) was heated under reflux in *n*-nonane (50 ml) in a nitrogen atmosphere for 4–5 hr. The progress of dehydrogenation was monitored by ir spectroscopy and was judged to be complete when the $\nu(\text{CO})$ band of VII at 1942 cm⁻¹ had disappeared and been replaced by the corresponding band of VIII at 1924 cm⁻¹. The solution was evaporated to dryness under reduced pressure, and the residue was washed with isopentane and dried

(49) A. J. Deeming and M. Underhill, *J. Organometal. Chem.*, **42**, C60 (1972).

(50) A. J. Deeming and M. Underhill, *J. Chem. Soc., Chem. Commun.*, 277 (1973).

(51) A. J. Canty, B. F. G. Johnson, and J. Lewis, *J. Organometal. Chem.*, **43**, C35 (1972).

(52) A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *ibid.*, **36**, C43 (1972).

(53) J. Halpern and B. R. James, *Can. J. Chem.*, **44**, 671 (1966).

(54) J. D. McClure, R. Owyang, and L. H. Slaugh, *J. Organometal. Chem.*, **12**, P8 (1968).

(55) R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 193 (1963).

(56) M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. A*, 1238 (1967).

in a stream of nitrogen. It was then dissolved in the minimum volume of dichloromethane (~3 ml) and treated with methanol (15 ml). On cooling overnight at 0° yellow crystals separated; these were washed with methanol and dried *in vacuo* (0.19 g, 95% based on VII). VIII could also be prepared by heating $\text{Ru}(\text{CO})_2(\text{SP})_2$ (V) in *n*-nonane for 5 hr or by heating the σ -bonded complex VI in *n*-nonane for 20–30 hr. Ir spectroscopy showed that VII was an intermediate in both cases (see text).

Preparation of Dihalocarbonylbis-1,4-[*o*-(diphenylphosphino)phenyl]-*cis*-2-buteneruthenium(II) Complexes, $\text{RuX}_2(\text{CO})\{o\text{-(C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CHCH}_2\text{C}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-}o\}$ [X = Cl (IX(i) and IX(ii)) or X = Br (X(i) and X(ii))] by Hydrogen Halide Addition to VIII. (i) A solution of VIII (0.1 g) in dichloromethane (5 ml) was degassed by passing nitrogen through it for several minutes and then treated with dry hydrogen chloride gas. The color changed from deep yellow to almost colorless over a period of 2 min, after which time the solution was again flushed with nitrogen. Solvent was removed under reduced pressure, and the residue was recrystallized from dichloromethane–methanol (1:4) to give colorless crystals IX(ii) ($\nu(\text{CO})$ 1990 cm^{-1} (Nujol)) which were washed with methanol

and dried *in vacuo* (yield, ~90%). On standing for several days the mother liquor deposited a mixture of colorless and yellow crystals, identified by their $\nu(\text{CO})$ bands at 1990 and 2015 cm^{-1} as IX(ii) and IX(i), respectively. These could not be separated owing to the ease with which IX(i) isomerized to IX(ii).

(ii) The procedure described above was repeated using hydrogen bromide in place of hydrogen chloride. The orange-brown complex initially isolated was X(i) ($\nu(\text{CO})$ 2010 cm^{-1} (Nujol)) (~90% yield). This isomerized at room temperature over a period of 3 weeks in dichloromethane to the more stable X(ii) ($\nu(\text{CO})$ 1989 cm^{-1}), as shown by nmr spectroscopy. The same process occurred more rapidly on three successive recrystallizations of X(i) from dichloromethane–methanol (1:4).

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Transition Metal Hydroborate Complexes. VI.¹ The Solid-State Structure of μ -Bis(cyanotrihydroborato)-tetrakis(triphenylphosphine)dicopper(I)

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Abstract: The structure of μ -bis(cyanotrihydroborato)-tetrakis(triphenylphosphine)dicopper(I) has been determined in a single-crystal X-ray diffraction study. The compound crystallizes in the space group $P2_1/n$ of the monoclinic system with four dimeric molecules per unit cell. The lattice parameters are $a = 18.100$ (1) Å, $b = 27.407$ (5) Å, $c = 13.615$ (1) Å, and $\beta = 104.43$ (1)°, with $\rho_{\text{obsd}} = 1.28$ (3) and $\rho_{\text{calcd}} = 1.27$ g cm^{-3} . From 2921 independent observed reflections collected by diffractometer the structure was solved and refined with the phenyl rings constrained as rigid bodies to a final value for the discrepancy index R_1 of 0.060. No crystallographic symmetry is imposed on the molecule. The H_3BCN^- ligands bridge the two copper atoms forming a ten-membered nonplanar ring, with a $\text{Cu}\cdots\text{Cu}$ distance of 5.637 (2) Å. Each quasitetrahedral copper atom is bonded to two triphenylphosphine ligands and to a hydrogen and a nitrogen atom from the different cyanotrihydroborate groups. The Cu–N distances are 1.96 (1) and 2.01 (1) Å. The average Cu–H distance of 1.86 ± 0.1 Å is similar to those found in related bis(triphenylphosphine)copper(I) hydroborate complexes. The structure is a rare example of a hydroborate ligand bonded by only one of its hydrogen atoms to a metal atom. The Cu–P distances are 2.262 (3), 2.242 (3), 2.272 (3), and 2.280 (3) Å, and the P–Cu–P angles are 124.8 (1) and 122.1 (1)°. The geometry of the coordinated H_3BCN ligand, determined for the first time, compares favorably to that of H_3CCN in related complexes. The local site symmetry at the boron atoms of the two cyanotrihydroborate ligands is distinctly different and can account for the appearance of two CN stretching bands in the infrared spectrum.

The cyanotrihydroborate anion, H_3BCN^- , was first isolated as the lithium salt in 1951,² and its utility as a selective organic reducing agent was later reported.^{3,4} Although the M–CNBH₃ linkage had been obtained from a solution of dicyanobis(*o*-phenanthroline)iron(II) that was allowed to react with diborane,⁵ complexes containing M–NCBH₃ bonds were unknown until recently.^{6–8}

(1) Part V: K. M. Melmed, D. Coucouvanis, and S. J. Lippard, *Inorg. Chem.*, **12**, 232 (1973).

(2) G. Wittig, *Justus Liebigs Ann. Chem.*, **573**, 209 (1951).

(3) G. Drefahl and E. Keil, *J. Prakt. Chem.*, **6**, 80 (1958).

(4) (a) R. F. Borch and H. D. Durst, *J. Amer. Chem. Soc.*, **91**, 3996 (1969); (b) R. F. Borch, M. D. Bernstein, and H. D. Durst, *ibid.*, **93**, 2897 (1971).

(5) D. F. Shriver, *J. Amer. Chem. Soc.*, **84**, 4610 (1962); **85**, 1405 (1963).

(6) S. J. Lippard and P. S. Welcker, *Chem. Commun.*, 515 (1970).

(7) P. C. Ford, *Chem. Commun.*, 7 (1971).

(8) L. Vaska, W. V. Miller, and B. R. Flynn, *Chem. Commun.*, 1615 (1971).

As discussed in a previous paper,⁹ interest in the title compound was initially generated from its infrared spectrum which strongly suggested the presence of both Cu–NCBH₃ and Cu–HBH₂CN type linkages. In particular, two possible dimeric structures were considered, and the present X-ray diffraction study was undertaken to determine which (if either) was the correct one. Additional incentive for this investigation was derived from the need to (1) test the remote possibility that the ligand had isomerized to form M–CNBH₃ bonds, (2) elucidate the nature of the copper-hydroborate attachment, and (3) determine the detailed molecular geometry of the cyanotrihydroborate anion, especially in its role as a bridging ligand. Also it was felt that structural information might help to assess the effect of the cyanide group on the coordinat-

(9) S. J. Lippard and P. S. Welcker, *Inorg. Chem.*, **11**, 6 (1972).