hydes. By contrast, the branched alkyls mainly give β-hydride elimination and only in part are transformed into aldehydes. Therefore, the branched aldehydes, to a larger extent than the linear isomers, arise from mono- and dideuteriostyrene, whose amounts increase with the increasing of substrate conversion and reaction temperature.

Experimental Section

Benzene was dried over molecular sieves and distilled under nitrogen. $Rh_4(CO)_{12}$ was prepared as reported in the literature.[13] GLC analyses were performed on a Dani 6800 gas chromatograph equipped with 2 m × 0.4 cm columns of 10% SE30 on 60/80 mesh Chromosorb WAW DCMS support or 5% UCON LB 550X on 60/80 mesh Chromosorb WAW DCMS support and a flame-ionization detector, nitrogen was used as the carrier gas. Preparative GLC was carried out on a Perkin-Elmer F21 instrument fitted with 3 m × 0.95 cm columns of 5% FFAP on 60/80 mesh Chromosorb A-NAW support.

Mass spectra were measured with a VG 70/70E spectrometer at an electron energy such that the $M - 1$ peak was undetectable (around 10 eV); the accelerating voltage was 6 kV and the emission current was 100 μA. GC-MS analyses of the deuterioformylation mixtures in selected ion monitoring mode were performed by the use of the same spectrometer coupled with a Dani 3800 gas chromatograph equipped with a SE30 silica capillary column (50 m × 0.53 mm).

^1H NMR spectra were recorded in CCl_4 solutions on a Varian VXR 300 spectrometer, operating at 300 MHz for ^1H. TMS was used as an internal standard.

Deuterioformylation of Styrene: General Procedure. Deuterioformylation of styrene, at partial and total substrate conversion, was carried out by following a general procedure previously described.[7] In a 50-mL evacuated stainless steel autoclave, a solution of styrene (2.01 g, 20 mmol) and $Rh_4(CO)_{12}$ (0.1 mg, 5.4×10^{-4} mmol) in benzene (5 mL) was introduced by suction. Carbon monoxide was introduced by the desired pressure; the autoclave was then rocked and heated to the reaction temperature, and deuterium was rapidly introduced to the desired total pressure. When the reaction started, drop in pressure was restored by injection of a carbon monoxide-deuterium mixture (1/1) from a high-pressure reservoir. Progress in the reaction was monitored by the pressure drop in the high-pressure container. When the gas absorption reached the value corresponding to the desired conversion to aldehydes, the autoclave was rapidly cooled, the reaction mixture was siphoned out, and GLC was used to determine the isomeric composition. The degree of styrene conversion was measured by GLC, using toluene as an internal standard. The reaction mixture was distilled first at atmospheric pressure and later at reduced pressure (0.4 mmHg), and the isomeric aldehydes were separated from styrene and solvent. Pure samples of unconverted styrene and α and β aldehydes were isolated by preparative GLC.

Deuterium Content of Residual Reaction Gas. The residual reaction gases were collected in evacuated Schlenk tubes closed with a rubber septum. A sample of the gas was taken through the septum by using a gastight syringe and directly introduced into the source of the mass spectrometer. The elium coming from the GLC column (m/z 4.0026) was used as a standard. The resolving power of the instrument was adjusted to about 2000: Under these conditions it was possible to distinguish among the peaks due to H_2 (m/z 2.0156), D (m/z 2.0141), coming from the fragmentation of D_2 and HD, HD (m/z 3.0219), and D_2 (m/z 4.0282). The MS spectra were recorded on UV paper, and the compositions of the gases were obtained by measuring the peak areas.

Acknowledgment. We wish to thank MPI (60%), Rome, for financial support.

Registry No. $PhCH{=}CH_2$, 100-42-5; $PhCD(CHD_2)CHO$, 136391-76-9; $PhCD(CH_2D)CHO$, 136391-77-0; $Ph(CHD)_2CHO$, 136391-78-1; $PhCHDCD_2CHO$, 136391-79-2; $Rh_4(CO)_{12}$, 19584-30-6; $PhCD(CD_3)CHO$, 136391-80-5; $PhCH{=}CHD$, 22139-13-5; D_2, 7782-39-0.

---

[13] McCleverty, J.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

Polyazolyl Chelate Chemistry. 3.[1]

(σ-Organyl)(tris(pyrazol-1-yl)borato)ruthenium Complexes

Nathaniel W. Alcock, Anthony F. Hill,* and Richard P. Melling

Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

Received January 25, 1991

The reactions of $K[HB(pz)_3]$ (pz = pyrazol-1-yl) with the coordinatively unsaturated σ-vinyl complexes $[Ru(CR{=}CHR)Cl(CO)(PPh_3)_2]$ (R = H, Me, C_6H_5) proceed with loss of a chloride and a phosphine ligand to provide the compounds $[Ru(CR{=}CHR)(CO)(PPh_3)\{HB(pz)_3\}]$ in high yield. Similar treatment of the complex $[Ru(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ leads to the related σ-aryl derivative $[Ru(C_6H_4Me\text{-}4)(CO)(PPh_3)\{HB(pz)_3\}]$. The α-(phenylethynyl)-*trans*-β-styryl complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}(CO)(PPh_3)\{HB(pz)_3\}]$ is obtained in high yield via the successive treatment of $[RuClH(CO)(PPh_3)_3]$ with 1,4-diphenyl-1,3-butadiyne and $K[HB(pz)_3]$. The molecular structure of $[Ru\{C(C{\equiv}CPh){=}CHPh\}(CO)(PPh_3)\{HB(pz)_3\}]$, determined by X-ray diffraction, can be described as pseudooctahedral with two enantiomeric forms in the asymmetric unit. The vinyl ligand is almost coplanar with the carbonyl ligand aligned in such a way as to maximize π-retrodative interactions.

Introduction

Research into the coordination chemistry of poly(pyrazol-1-yl)borates has focused on the first-row transition metals and group 6.[2] The chemistry of tris(pyrazol-1-yl)borato complexes of the second- and third-transition series and in particular that of group 8[3-7] remains less

---

[1] For part II, see: Cartwright, J.; Harman, A.; Hill, A. F. *J. Organomet. Chem.* **1989**, *396*, C31.

[2] Trofimenko, S. J. *Prog. Inorg. Chem.* **1986**, *34*, 115.

[3] Bruce, M. I.; Sharrocks, D. N.; Stone, F. G. A. *J. Organomet. Chem.* **1971**, *31*, 269. Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2820.

[4] McNair, A. M.; Boyd, D. C.; Mann, K. R. *Organometallics* **1986**, *5*, 303.

Table I. Infrared Data for Complexes Containing $Ru(CO)(PPh_3)\{HB(pz)_3\}$ ([Ru])

	infrared data, cm^{-1}			
		Nujol[b]		
compd	CH_2Cl_2[a] ν(CO)	ν(CO)	ν(BH)	other
[Ru](C_6H_4Me-4) (1)	1942	1941 vs	2462 m	1499 m, 1407 s, 1395 s, 1308 s, 1214 vs, 1118 vs, 1048 vs, 982 w, 978 w, 801 m
[Ru]($CH{=}CH_2$) (2)	1941	1927 vs	2500 m	1555 s, 1502 m, 1403 s, 1592 s, 1311 s, 1304 s, 1255 m, 1219 s, 1209 s, 1111 vs, 1048 vs, 982 w, 978 w, 920 vw, 888 vw, 863 s
[Ru](CMe=CHMe) (3)	1937	1921 vs	2458 m	1565 w, 1492 w, 1403 s, 1392 s, 1313 s, 1212 vs, 1204 s, 1112 vs, 1043 vs, 978 m, 921 vw, 888 vw
[Ru](CPh=CHPh) (4)	1931	1940 vs	2450 m	1588 w, 1503 w, 1408 m, 1396 m, 1309 s, 1214 vs, 1114 s, 1048 vs, 978 w, 922 w, 878 w, 845 w
[Ru]{$C(C{\equiv}CPh){=}CHPh$} (5)	1954	1956 vs, 1942 vs	2464 m	2157 m, 1593 m, 1397 m, 1378 s, 1308 s, 1213 vs, 1116 vs, 1048 vs, 981 w, 913 vw
	2160 [$\nu(C{\equiv}C)$]			

[a] Data were obtained from dichloromethane solutions in the range 2200–1500 cm^{-1}. [b] Data were obtained from Nujol mulls between KBr disks in the range 4000–400 cm^{-1}; bands due to coordinated triphenylphosphine were omitted.

developed, though there is no obvious reason why this should be the case. This report is concerned with the synthesis of (σ-organyl)(tris(pyrazol-1-yl)borato)ruthenium complexes and describes high-yield routes to aryl and σ-vinyl derivatives, an example of the latter being the subject of a crystal structure determination. Since a preliminary report of this work, important contributions to the hydrotris(pyrazolyl)borate chemistry of ruthenium have appeared describing syntheses of the complex $[Ru_2(CO)_4\{HB(pz)_3\}_2]$[8] and the cation $[Ru(H_2O)_3\{HB(pz)_3\}]^+$.[9]

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of prepurified dinitrogen by using conventional Schlenk-tube techniques. Solvents were purified by distillation from an appropriate drying agent [ethers, paraffins, benzene, and toluene from sodium/potassium alloy with benzophenone as indicator; halocarbons and acetonitrile from CaH_2 and alcohols from the corresponding alkoxide].

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WH-400 or Perkin-Elmer R34 NMR spectrometer and calibrated against internal Me_4Si (^1H), internal $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P). Infrared spectra were recorded by using a Perkin-Elmer 1720-X FT infrared spectrometer. FAB mass spectrometry was carried out by using a Kratos MS80 mass spectrometer (nitrobenzyl alcohol matrix). Light petroleum refers to that fraction of boiling point 40–60 °C. The complexes $[Ru(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$,[10] $[Ru(CR{=}CHR)Cl(CO)(PPh_3)_2]$,[11] and $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$[12] are described elsewhere. Data for the new complexes are given in Tables I–III.

Table II. ^1H NMR Data for Complexes[a] Containing $Ru(CO)(PPh_3)\{HB(pz)_3\}$ ([Ru])

compd	$\delta(^1H)$
[Ru](C_6H_4Me-4) (1)	2.26 (s, 3 H, CH_3), 5.90, 5.94, 6.04 (m, × 3, 3 H, $C_3H_3N_2$), 6.59, 6.90, 7.18, 7.39, 7.63, 7.68, 7.79 (m × 6, 25 H, C_6H_5 and $C_3H_3N_2$)
[Ru]($CH{=}CH_2$) (2)	5.44, 5.52 (m × 2, 3 H, $CHCH_2$], 6.05, 6.24, 6.73, 6.80 (m, × 4, 3 H, $C_3H_3N_2$), 7.21, 7.57, 7.68, 7.84 (m × 4, 21 H, C_6H_5 and $C_3H_3N_2$)
[Ru](CMe=CHMe) (3)	1.58 (s, 3 H, $RuCCH_3$), 1.64 [d, 3 H, $=CHCH_3$, $J(HH) = 7$ Hz], 4.92 [q, 1 H, $CHCH_3$, $J(H)) = 7$ Hz], 5.89, 6.15, 6.79, 6.86 (m × 4, 3 H, $C_3H_3N_2$), 7.25, 7.66 (m × 2, C_6H_5 and $C_3H_3N_2$)
[Ru](CPh=CHPh) (4)	5.35 [s (br), 1 H, CHPh], 5.66, 5.83, 6.03, 6.15, 6.22, 7.02, 7.26, 7.55, 7.65, 7.96, 8.04 (m × 11, 34 H, C_6H_5 and $C_3H_3N_2$)
[Ru]{$C(C{\equiv}CPh){=}CHPh$} (5)	5.92, 6.01, 6.15, 6.92, 7.09–7.40, 7.63–7.80 (m × 6, no unequivocal assignments made)

[a] From saturated solutions of the complex in $CDCl_3$ at ambient temperature. Chemical shifts are given relative to internal Me_4Si (0.00 ppm).

Table III. FAB-MS Data for Complexes[a] Containing $Ru(CO)(PPh_3)\{HB(pz)_3\}$ ([Ru])

compd	m/z, assgnt
[Ru](C_6H_4Me-4) (1)	697, $[M]^+$; 605 $[M - C_7H_7]^+$; 676, $[M - C_7H_7 - CO]^+$; 391, $[Ru(CO)PPh_3]^+$
[Ru]($CH{=}CH_2$) (2)	634, $[M]^+$; 605, $[[M - C_2H_2]^+$; 577, $[M - C_2H_2 - CO]^+$; 391, $[Ru(CO)PPh_3]^+$; 363, $[RuPPh_3]^+$
[Ru](CMe=CHMe) (3)	605, $[M - C_4H_6]^+$; 576, $[M - C_4H_6 - CO]^+$; 391, $[Ru(CO)PPh_3]^+$; 363, $[RuPPh_3]^+$
[Ru](CPh=CHPh) (4)	784, $[M]^+$; 605, $[M - PhC{=}CHPh]^+$; 577, $[M - PhC{=}CHPh - CO]^+$; 363, $[RuPPh_3]^+$; 263, $[HPPh_3]^+$

[a] Measured from nitrobenzyl alcohol matrices.

Syntheses. $[Ru(CPh{=}CHPh)(CO)(PPh_3)\{HB(pz)_3\}]$ (4). $[RuCl(CPh{=}CHPh)(CO)(PPh_3)_2]$ (0.87 g, 1.00 mmol) and $K[HB(pz)_3]$ (0.26 g, 1.03 mmol) were placed in a nitrogen-flushed Schlenk tube, which was then evacuated thrice, backfilling with nitrogen each time. Freshly distiled dichloromethane (30 cm^3) was then added by syringe and the reaction mixture stirred magnetically for 15 min. Petroleum ether (30 cm^3) was then added and the mixture stirred for a further 15 min, after which the precipitated potassium chloride was removed by filtration through diatomaceous earth. The solvent volume was reduced to ca. 10 cm^3 under reduced pressure and the white product isolated by

---

(5) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E.; *Organometallics* **1986**, *5*, 2199. Albers, M. O.; Crosby, S. F. A.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2015. Albers, M. O.; Oosthuisen, H. E.; Robinson, D. J.; Shaver, A.; Singleton, E. *J. Organomet. Chem.* **1985**, *282*, C49.

(6) Restivo, R. J.; Ferguson, G.; O'Sullivan, D. J.; Lalor, F. J. *Inorg. Chem.* **1975**, *14*, 3046. Restivo, R. J.; Ferguson, G. *J. Chem. Soc., Chem. Commun.* **1973**, 847, O'Sullivan, V.; Lalor, F. J. *J. Organomet. Chem.* **1973**, *57*, C58.

(7) Hiraki, K.; Ochi, N.; Kitamura, T.; Sasada, Y.; Shinoda, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2356.

(8) Llobet, A.; Hodgson, D. J.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 3760.

(9) Steyn, M. M. deV.; Singleton, E.; Hietkamp, S.; Liles, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 2991.

(10) (a) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1. (b) Ricard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1990**, *389*, 375.

(11) (a) Torres, M. R.; Santos, A.; Ros, J.; Solans, X. *Organometallics* **1987**, *6*, 1091. (b) Torres, M. R.; Vegas, A.; Santos, A. *J. Organomet. Chem.* **1986**, *309*, 169. (c) Loumrhari, H.; Ros, J.; Torres, M. R.; Perales, A. *Polyhedron* **1990**, *9*, 907. (d) Torres, M. R.; Perales, A.; Ros, J. *Organometallics* **1988**, *7*, 1223. (e) Torres, M. R.; Vegas, A.; Santos, A. *J. Organomet. Chem.* **1987**, *326*, 413.

(12) Hill, A. F.; Melling, R. P. *J. Organomet. Chem.* **1990**, *396*, C22.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for the Complex $\mathrm{[Ru\{C(C{\equiv}CPh){=}CHPh\}(CO)(PPh_3)\{HB(pz)_3\}]}$ (5)[a] (Esd's Given in Parentheses)

Ru(1)–P(1)	2.341 (4)	Ru(1)–N(111)	2.117 (11)
Ru(1)–N(121)	2.17 (1)	Ru(1)–N(131)	2.184 (10)
Ru(1)–C(11)	1.85 (1)	Ru(1)–C(12)	2.090 (12)
C(11)–O(1)	1.09 (2)		
C(12)–C(13)	1.40 (2)	C(12)–C(15)	1.374 (19)
C(13)–C(14)	1.22 (2)	C(14)–C(111)	1.383 (19)
C(15)–C(121)	1.51 (2)		
P(1)–Ru(1)–N(111)	176.3 (3)	P(1)–Ru(1)–N(121)	92.4 (3)
P(1)–Ru(1)–N(131)	95.1 (3)	P(1)–Ru(1)–C(11)	95.2 (5)
P(1)–Ru(1)–C(12)	91.4 (4)	N(111)–Ru(1)–N(121)	84.1 (4)
N(111)–Ru(1)–N(131)	85.5 (4)	N(111)–Ru(1)–C(11)	88.4 (5)
N(111)–Ru(1)–C(12)	87.9 95)	N(121)–Ru(1)–N(131)	84.9 (4)
N(121)–Ru(1)–C(11)	172.4 (5)	N(121)–Ru(1)–C(12)	92.0 (4)
N(131)–Ru(1)–C(11)	93.3 (5)	N(131)–Ru(1)–C(12)	172.9 (4)
C(11)–Ru(1)–C(12)	88.9 (5)	C(11)–Ru(1)–C(12)	175 (1)
Ru(1)–C(12)–C(13)	118.8 (9)	Ru(1)–C(12)–C(15)	122 (1)
C(12)–C(15)–C(121)	131 (1)	C(12)–C(13)–C(14)	175 (2)
C(13)–C(14)–C(111)	173 (2)		

[a] Data given for molecule based on Ru(1). Structural parameters for the molecule based on Ru(2) are essentially identical and have been submitted as supplementary material and to the Cambridge Crystallographic Data Base.

filtration and washed twice with petroleum ether (2 × 10 cm^3). Yield: 0.70 g (89%). The complex could be further purified by recrystallization from dichloromethane/petroleum ether mixtures at −30 °C. Anal. Found: C, 64:1; H, 4.5; N, 10.2 Calcd for $\mathrm{C_{42}H_{36}BON_6PRu}$: C, 64.4; H, 4.6; N, 10.7.

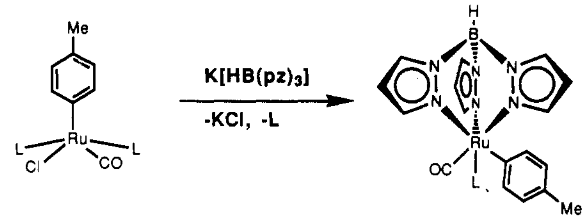
$\mathrm{[RuR(CO)(PPh_3)\{HB(pz)_3\}]}$ [R = $\mathrm{C_6H_4Me}$-4 (1), $\mathrm{CH{=}CH_2}$ (2), $\mathrm{CMe{=}CHMe}$ (3), $\mathrm{C(C{\equiv}CPh){=}CHPh}$ (5)] were prepared in comparable yields [84 (1), 92 (2), 72 (3), and 84% (5) based on 0.50 mmol of $\mathrm{[RuRCl(CO)(PPh_3)_2]}$] in a manner completely analogous to that described above for the diphenyl derivative by employing the complexes $\mathrm{[RuRCl(CO)(PPh_3)_2]}$. All the compounds are colorless and are obtained as microcrystals, which may be recrystallized from a mixture of dichloromethane and light petroleum at −30 °C. Data for 1 are as follows. Anal. Found: C, 59.9; H, 4.2; N, 12.2. Calcd for $\mathrm{C_{35}H_{32}BON_6PRu}$: C, 60.4; H, 4.6; N, 12.1. Data for 2 are as follows. Anal. Found: C, 57.1; H, 4.7; N, 13.1. Calcd for $\mathrm{C_{30}H_{28}BON_6PRu}$: C, 57.1; H, 4.5; N, 13.3. Data for 3 are as follows. Anal. Found: C, 57.7; H, 4.5; N, 13.1. Calcd for $\mathrm{C_{35}H_{32}BON_6PRu}$: C, 58.3; H, 4.9; N, 12.7. Data for 5 are as follows. Anal. Found: C, 65.1; H, 4.4; N, 10.0. Calcd for $\mathrm{C_{35}H_{32}BON_6PRu}$: C, 65.4; H, 4.5; N, 10.4.

Crystal Data, X-ray Data Collection, and Structural Determination. Yellow prisms of the title complex (5) were grown from dichloromethane/2-propanol by solvent vapor diffusion. That chosen for data collection (ca. 0.13 × 0.12 × 0.36 mm) was mounted on a glass fiber. Diffracted intensities were collected (θ-2θ scans) at 298 K in the range $3° < 2\theta < 45°$, on a Nicolet P3m four-circle diffractometer. Of 10734 unique reflections, 6484 had $F \geq 4\sigma(F)$, and only these data were used in the solution and refinement of the structure. Corrections were applied for Lorentz, polarization, and X-ray absorption effects.

Crystal data for $\mathrm{[Ru\{C(C{\equiv}CPh){=}CHPh\}(CO)(PPh_3)\{HB(pz)_3\}]}$ (5): $\mathrm{C_{44}H_{38}BN_6OPRu}$, $M_r = 826.1$, monoclinic, $a = 19.641$ (8) Å, $b = 18.569$ (10) Å, $c = 22.701$ (8) Å, $\beta = 96.20$ (3)°, $U = 8231$ (5) Å^3, $Z = 8$, $D_c = 1.34$ g cm^{-3}, $F(000) = 3312$, space group = $P2_1/c$, Mo Kα X-radiation ($\lambda = 0.71073$ Å, graphite monochromator), μ(Mo Kα) = 0.45 mm^{-1}.

The structure was solved, and all non-hydrogen atoms were located, by conventional heavy-atom and difference Fourier methods, which indicated that there were two molecules in the asymmetric unit. Phenyl and pyrazolyl hydrogen atoms were included in calculated positions (C–H = 0.96 Å) with fixed isotropic thermal parameters. The difference Fourier map showed two peaks, the refined occupancy of which converged to 0.62 (unfixed at 0.10 Å^2), assumed to be the oxygen atoms of crystal water. All non-hydrogen atoms (except these oxygen atoms) were refined anisotropically (blocked least squares; 853 parameters), the refinement converging at $R = 0.076$ ($R_w = 0.081$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000328|F|^2]$. The only residual electron density peaks on the final difference synthesis of singificant height (1.1 e Å^{-3}) were near the solvent water. Scattering factors and corrections for anomalous dispersion were taken from ref 13. All calculations were carried out by using a DEC micro-Vax II computer with the SHELXTL PLUS suite of programs.[14] Selected bond lengths and angles and atomic coordinates are given in Tables IV and V; thermal parameters and structure factor values have been deposited as supplementary material.

Scheme I



Results and Discussion

The coordinatively unsaturated σ-aryl complex $\mathrm{[Ru(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]}$[10] and the σ-vinyl complexes $\mathrm{[Ru(CR{=}CHR)Cl(CO)(PPh_3)_2]}$ (R = H, Ph, $\mathrm{CH_3}$)[11] are unusually robust and serve as useful starting materials for a wide range of complexes.[12,15–18] The halide ligand in $\mathrm{[RuCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2]}$ is labile,[10] suggesting the potential accessibility of two vacant coordination sites, and it therefore appeared reasonable that these complexes might serve as useful precursors for developing organoruthenium chemistry wherein the ruthenium was ligated by the *fac*ially tridentate tris(pyrazolyl)borate ligand. The synthesis of a cyanoethyl complex $\mathrm{[Ru\{CH(CN)CH_3\}(CO)(PPh_3)\{HB(pz)_3\}]}$ from the chlorobridged dimer[7] $\mathrm{[Ru_2(\mu\text{-}Cl)_2\{CH(CN)CH_3\}_2(CO)_2(PPh_3)_4]}$ has been reported by Hiraki et al.

Treatment of the virtually insoluble bright red complex $\mathrm{[Ru(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]}$ with 1 equiv of $\mathrm{K[HB(pz)_3]}$ in dichloromethane resulted in the slow dissolution of the organometallic complex and formation of a pale yellow solution and a colorless precipitate (KCl). The crystallization of the potassium chloride was completed by the addition of an equal volume of petroleum ether allowing the salt to be removed by filtration through diatomaceous earth. Concentration of the solvent volume under reduced pressure resulted in the formation of white crystals of the complex $\mathrm{[Ru(C_6H_4Me\text{-}4)(CO)(PPh_3)\{HB(pz)_3\}]}$ (1) (Scheme I).

The molecular composition of the complex was apparent from spectroscopic data: Infrared activity at 1941 cm^{-1} (Nujol mull) corresponding to ν(CO) indicated that a phosphine ligand and not the carbonyl ligand had been eliminated and that the aryl group had failed to migrate onto the carbonyl ligand. The appearance of one singlet resonance in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum indicates that only one phosphine remains bound to ruthenium. The gross

---

(13) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

(14) Sheldrick, G. M. SHELXTL programs for use with the Nicolet X-ray system. Revision 5.1, 1986.

(15) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Shepard, W. E. B.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1987**, 563.

(16) Herberhold, M.; Hill, A. F. *J. Organomet. Chem.* **1990**, *395*, 327; **1989**, *377*, 151; **1988**, *353*, 243.

(17) Herberhold, M.; Hill, A. F. *J. Organomet. Chem.* **1990**, *315*, 105. Gieren, A.; Ruiz-Perez, C.; Hübner, T.; Herberhold, M.; Hill, A. F. *J. Chem. Soc., Dalton Trans.* **1988**, 1693.

(18) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1978**, *157*, C27; **1979**, *182*, C46.

Table V. Atomic Positions ($\times 10^4$) for [Ru{C(C≡CPh)=CHPh}(CO)(PPh_3){HB($pz)_3$}]

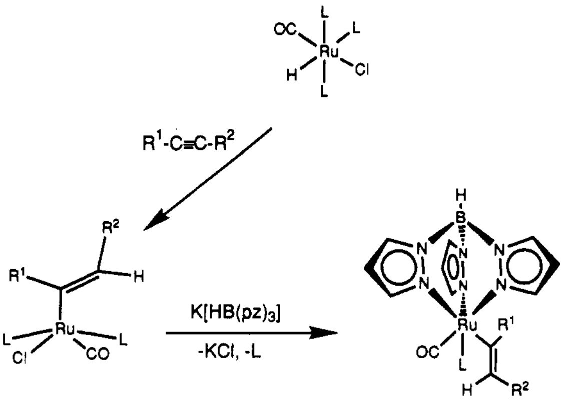
atom	x	y	z	atom	x	y	z
Ru(1)	6662.0 (5)	7051.4 (5)	5541.1 (5)	Ru(2)	3396.7 (5)	4081.7 (5)	9198.6 (4)
P(1)	5758 (2)	7287 (2)	6109 (2)	P(2)	4165.2 (16)	3829.1 (18)	8504.7 (14)
B(1)	7553 (8)	8219 (8)	4907 (7)	B(2)	2829 (8)	2866 (10)	10048 (7)
O(1)	6015 (6)	5834 (5)	4858 (5)	O(2)	4075 (5)	5418 (5)	9712 (4)
N(111)	7520 (5)	6883 (6)	5065 (5)	N(211)	2689 (5)	4171 (5)	9839 (4)
N(112)	7811 (6)	7473 (7)	4811 (5)	N(212)	2557 (5)	3609 (6)	10168 (5)
N(121)	7269 (5)	7938 (5)	5943 (5)	N(221)	2803 (5)	3143 (5)	8945 (5)
N(122)	7590 (5)	8355 (5)	5572 (4)	N(222)	2628 (6)	2698 (6)	9388 (5)
N(131)	6330 (5)	7833 (5)	4847 (4)	N(231)	3960 95)	3415 (5)	9865 (4)
N(132)	6803 (5)	8275 (6)	4651 (4)	N(232)	3610 (5)	2912 (6)	10140 (5)
C(11)	6232 (7)	6283 (8)	5129 (6)	C(21)	3829 (6)	4897 (7)	9496 (5)
(C12)	7102 (6)	6318 (7)	6172 (6)	C(22)	2762 (6)	4717 (6)	8595 (5)
C(13)	6769 (8)	5660 (8)	6246 (6)	C(23)	3095 (7)	5382 (8)	8436 (6)
C(14)	6456 (9)	5090 (9)	6268 (8)	C(24)	3373 (7)	5942 (7)	8320 (6)
C(15)	7710 (8)	6464 (8)	6510 (7)	C(25)	2114 (6)	4556 (7)	8404 (6)
C(111)	6175 (5)	4413 (5)	6336 (5)	C(211)	3679 (5)	6595 (4)	8177 (4)
C(112)	5480 (5)	4297 (5)	6160 (5)	C(212)	4386 (5)	6623 (4)	8151 (4)
C(113)	5178 (5)	3638 (5)	6282 (5)	C(213)	4696 (5)	7271 (4)	8012 (4)
C(114)	5571 (5)	3094 95)	6578 (5)	C(214)	4299 (5)	7892 (4)	7899 (4)
C(115)	6267 (5)	3209 (5)	6753 (5)	C(215)	3592 (5)	7865 (4)	7925 (4)
C(116)	6569 (5)	3869 (5)	6632 (5)	C(216)	3282 (5)	7217 (4)	8064 (4)
C(121)	8071 (5)	6085 (6)	7046 (4)	C(221)	1629 (4)	4935 (5)	7976 (4)
C(122)	7828 (5)	5478 (6)	7325 (4)	C(222)	1789 (4)	5529 (5)	7637 (4)
C(123)	8203 (5)	5194 (6)	7829 (4)	C(223)	1282 (4)	5849 (5)	7244 (4)
C(124)	8819 (5)	5515 (6)	8055 (4)	C(224)	615 (4)	5575 (5)	7190 (4)
C(125)	9062 (5)	6122 (6)	7776 (4)	C(225)	455 (4)	4981 (5)	7529 (4)
C(126)	8688 (5)	6406 (6)	7272 (4)	C(226)	962 (4)	4661 (5)	7922 (4)
C(131)	5256 (4)	8083 (3)	5890 (4)	C(231)	4668 (4)	3030 (4)	8714 (4)
C(132)	4541 (4)	8076 (3)	5830 (4)	C(232)	5384 (4)	3045 (4)	8769 (4)
C(133)	4176 (4)	8703 (3)	5660 (4)	C(233)	5757 (4)	2438 (4)	8979 (4)
C(134)	4526 (4)	9338 (3)	5550 (4)	C(234)	5415 (4)	1816 (4)	9135 (4)
C(135)	5242 (4)	9345 (3)	5610 (4)	C(235)	4699 (4)	1801 (4)	9081 (4)
C(136)	5607 (4)	8717 (3)	5780 (4)	C(236)	4326 (4)	2408 (4)	8870 (4)
C(141)	5094 (4)	6597 (4)	6121 (4)	C(241)	4850 (3)	4478 (4)	8389 (3)
C(142)	4785 (4)	6356 (4)	5574 (4)	C(242)	5199 (3)	4812 (4)	8883 (3)
C(143)	4253 (4)	5852 (4)	5549 (4)	C(243)	5752 (3)	5269 (4)	8816 (3)
C(144)	4029 (4)	5589 (4)	6072 (4)	C(244)	5955 (3)	5392 (4)	8254 (3)
C(145)	4338 (4)	5829 (4)	6619 (4)	C(245)	5606 (3)	5058 (4)	7759 (3)
C(146)	4871 (4)	6333 (4)	6643 (4)	C(246)	5053 (3)	4601 (4)	7827 (3)
C(151)	6019 (4)	7466 (5)	6901 (3)	C(251)	3806 (4)	3620 (5)	7745 (3)
C(152)	5940 (4)	8160 (5)	7124 (3)	C(252)	3929 (4)	2956 (5)	7483 (3)
C(153)	6247 (4)	8341 (5)	7688 (3)	C(253)	3646 (4)	2812 (5)	6095 (3)
C(154)	6632 (4)	7827 (5)	8028 (3)	C(254)	3241 (4)	3331 (5)	6588 (3)
C(155)	6711 (4)	7132 (5)	7805 (3)	C(255)	3118 (4)	3995 (5)	6850 (3)
C(156)	6405 (4)	6951 (5)	7241 (3)	C(256)	3401 (4)	4139 (5)	7428 (3)
C(161)	7823 (8)	6307 (9)	4924 (7)	C(261)	2367 (6)	4730 (8)	10068 (7)
C(162)	8331 (9)	6476 (10)	4575 (8)	C(262)	2045 (7)	4494 (10)	10535 (7)
C(163)	8304 (8)	7239 (10)	4540 97)	C(263)	2169 (7)	3800 (8)	10580 (6)
C(171)	7460 (6)	8166 (7)	6478 (6)	C(271)	2526 (6)	2867 (8)	8422 (6)
C(172)	7905 (6)	8724 (7)	6484 (7)	C(272)	2160 (8)	2213 (8)	8520 (7)
C(173)	7984 (7)	8833 (7)	5898 (7)	C(273)	2223 (7)	2141 (8)	9127 (9)
C(181)	5745 (7)	8003 (7)	4531 (6)	C(281)	4607 (7)	3366 (7)	10080 (5)
C(182)	5826 (8)	8526 (7)	4127 (6)	C(282)	4700 (8)	2831 (9)	10484 (6)
C(183)	6510 (8)	8695 (7)	4221 (6)	C(283)	4050 (8)	2546 (8)	10508 (6)
				O(001)	4191 (10)	368 (10)	988 (8)
				O(002)	3069 (9)	657 (10)	550 (8)

composition was finally confirmed by FAB mass spectrometry, which showed peaks due to the molecular ion and loss of the organyl ligand followed by carbonyl, borate, and finally phosphine groups, in addition to a peak due to the [Ru(CO)(PPh_3)]$^+$ fragment.

The addition of carbon monoxide to solutions of [Ru(C_6H_4Me-4)Cl(CO)($PPh_3)_2$] has been shown to produce the dicarbonyl complex [RuCl(C_6H_4Me-4)$(CO)_2(PPh_3)_2$], which is in equilibrium with the toluoyl tautomer [RuCl{C(O)C_6H_4Me-4}(CO)($PPh_3)_2$].[10] Treating solutions of the complex [Ru(C_6H_4Me-4)(CO)(PPh_3){HB($pz)_3$}] (4) with carbon monoxide at atmospheric pressure, however, fails to produce any of the corresponding toluoyl complex [Ru{C(O)C_6H_4Me-4}(CO)(PPh_3){HB($pz)_3$}] (monitored by solution infrared spectroscopy).

σ-Vinyl Complexes. Santos and co-workers have recently described the synthesis of the coordinatively unsaturated σ-vinyl complexes [RuCl(CR=CHR)(CO)($PPh_3)_2$] (R = H, CH_3, Ph) by cis addition of the ruthenium hydrogen bond of [RuClH(CO)($PPh_3)_3$] to a variety of alkynes with concomitant loss of a phosphine ligand.[11] The *trans*-β-styryl derivative is also accessible from the reaction of [RuClH(CO)($PPh_3)_3$] with [Hg(CH=CHPh)$_2$].[10b] The synthesis of the parent complex [RuCl(CH=CH_2)(CO)($PPh_3)_2$] was reported to be complicated by subsequent ethyne insertions leading to uncharacterized poly(enyl) derivatives;[11] however, we find that, by carrying out the reaction at room temperature with 1 atm of ethyne, it is possible to obtain high yields of the desired uncontaminated product. Furthermore, the reaction may also be extended to include 1,4-diphenyl-1,3-butadiyne whereby a complex of the α-(phenylethynyl)-σ-*trans*-β-styryl ligand is produced.[12] These complexes readily coordinate neutral ligands paralleling the reactivity

Scheme II



R^1 = H	Ph	Me	C≡CPh
R^2 = H	Ph	Me	Ph

L = PPh$_3$

of the *p*-tolyl derivative described above.

Treating [RuCl(CR=CHR)(CO)(PPh$_3$)$_2$] with K[HB(pz)$_3$] in dichloromethane under conditions identical with those described above provides the near colorless pseudooctahedral complexes [Ru(CR=CHR)(CO)(PPh$_3$){HB(pz)$_3$}] [R = H (**2**), CH$_3$ (**3**), Ph (**4**)] as the only organometallic products (Scheme II). As with the *p*-tolyl derivative, the infrared spectra show that one phosphine ligand is lost in the reactions, leaving a *fac*ial arrangement of σ-organyl, phosphine, and carbonyl ligands. The FAB mass spectra of the complexes shows sequential loss of σ-organyl, tris(pyrazolyl)borate, carbonyl, and finally phosphine ligands from the ruthenium center.

A similar reaction is observed for the α-(phenylethynyl)-σ-*trans*-β-styryl derivative leading to the formation of the yellow complex [Ru{C(C≡CPh)=CHPh}(CO)(PPh$_3$){HB(pz)$_3$}] (**5**) (Scheme II).

The latter complex provided crystals suitable for an X-ray diffraction study (see Experimental Section), the results of which are summarized in Tables IV and V and Figure 1. The $^{13}C\{^1H\}$ NMR spectrum of **5** was measured, and while generally unremarkable, the signals for the carbon atoms bound to ruthenium show ^2J couplings to phosphorus of 14.8 (CO, δ = 205.7) and 11.8 Hz (vinyl, δ = 142.1 ppm) consistent with coordination of these ligands cis to the phosphine.

Description of the Structure of the Complex [Ru{C(C≡CPh)=CHPh}(CO)(PPh$_3$){HB(pz)$_3$}]. If we consider the hydrotris(pyrazolyl)borate ligand to act as one group bound to ruthenium, then the expected structure would involve ruthenium ligated by four different groups and therefore this center would exist in two enantiomeric forms. Indeed the asymmetric unit of the unit cell contains two molecules of the complex that are approximate mirror images with some minor variations presumably due to crystal packing forces. The following dimensions and discussion are for the molecule based on Ru(1).

The coordination geometry is approximately octahedral with all angles at ruthenium being between 84 and 95°. The vinyl ligand lies almost coplanar with the ruthenium carbonyl linkage with a C(15)–C(12)–Ru(1)–C(11) dihedral angle of 153.8 (2)°. The three Ru–N bond lengths show some minor variation, 2.117 (11), 2.168 (10), and 2.184 (10) Å, the longest being observed for that trans to the σ-vinyl ligand and the shortest being that trans to the phosphine.

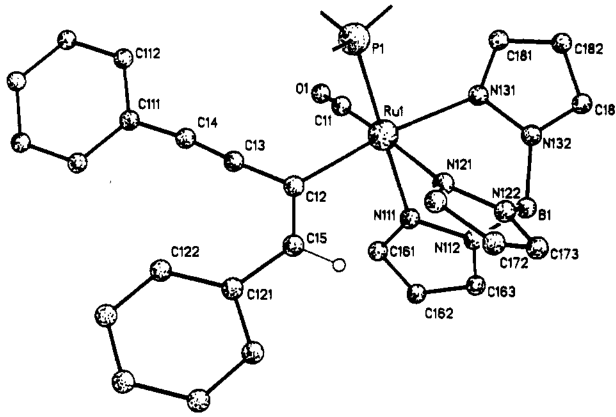


Figure 1. Molecular structure of [Ru{C(C≡CPh)=CHPh}(CO)(PPh$_3$){HB(pz)$_3$}] [enantiomer based on Ru(1)]. Phosphine phenyl groups are omitted for clarity.

These variations are presumably of steric origin, though the σ-vinyl ligand might be expected to exert some trans influence.

The orientation of isoelectronic acyl ligands in the related system [Fe{C(O)R}(CO)(PPh$_3$)(η-C$_5$H$_5$)] has been studied in detail because of its implication in stereoselective synthesis,[19] and this is normally found to be such that the acyl and carbonyl ligands are coplanar. The hydrotris(pyrazolyl)borate ligand tends to result in a more octahedral geometry at the metal than the cyclopentadienyl ligand, and accordingly, the situation becomes clearly one of competition of the vinyl π*-acceptor orbital with either a phosphine or carbonyl ligand depending on which of the two orthogonal d orbitals with which it aligns. Thus by assumption of an orientation coplanar with the carbonyl ligand, retrodative bonding with the d orbital that also interacts with the phosphine will be maximized. The preference for the α-ethynyl substituent to line up cisoid to the carbonyl rather than the alternative arrangement with the vinyl group in this position is presumably steric in origin although secondary orbital interactions between acetylenic and carbonyl orbitals should perhaps not be ruled out. The variations in C–C bond lengths within the vinyl moiety, as illustrated in Figure 1, are as expected for the η^1-α-(phenylethynyl)-*trans*-β-styryl ligand, which has been structurally characterized in the complex [Ru{C(C≡CPh)=CHPh}(O$_2$CCF$_3$)(CO)$_2$(PPh$_3$)$_2$].[20] This ligand has also been observed to coordinate in a trihapto manner given a suitably unsaturated metal–ligand system.[21-23]

Conclusions

A facile entry into air-stable organometallic ruthenium tris(pyrazol-1-yl)borate chemistry has been developed for simple σ-vinyl and σ-tolyl derivatives. The compounds described herein were routinely prepared under anaerobic conditions; however, solutions of the complexes appear to be indefinitely stable toward air and this should facilitate the wider exploitation of their chemistry currently underway in this laboratory.

---

(19) Blackburn, B. K.; Davies, S. G.; Sutton, I. C. H.; Whittaker, M. *Chem. Soc. Rev.* **1988**, *17*, 147.

(20) Dobson, A.; Moore, D. S.; Robinson, S. D.; Hursthouse, M.; New, L. *J. Organomet. Chem.* **1979**, *177*, C8; *Polyhedron* **1985**, *4*, 1119.

(21) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247.

(22) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378.

(23) We have structurally characterized the salt [Ru{η^3-PhCHCCCPh}(CO)$_2$(PPh$_3$)$_2$]PF$_6$: Alcock, N. W.; Hill, A. F.; Thompsett, A. R. Manuscript in preparation.

Acknowledgment. We wish to thank Johnson Matthey Ltd for the generous loan of ruthenium salts.

Registry No. 1, 130807-04-4; 2, 130807-02-2; 3, 130829-14-0; 4, 130807-03-3; 5, 130807-05-5; [RuCl(CPh$=$CHPh)(CO)(PPh$_3$)$_2$], 109800-34-2; [RuCl(CCH$_3$$=$CHCH$_3$)(CO)(PPh$_3$)$_2$], 128298-72-6; [RuCl(CH$=CH_2$)(CO)(PPh$_3$)$_2$], 114882-66-5; [RuCl(CPh$=$CHC$\equiv$CPh)(CO)(PPh$_3$)$_2$], 131345-47-6; K[HB(pz)$_3$], 18583-60-3.

Supplementary Material Available: Tables of atom coordinates, isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and calculated H atom coordinates (10 pages); a table of calculated and observed structure factors (39 pages). Ordering information is given on any current masthead page.

Reactions of [RuClH(CO)(BSD)(PPh$_3$)$_2$] (BSD = Benzo-2,1,3-selenadiazole) with Alkynes

Michael C. J. Harris and Anthony F. Hill*

Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

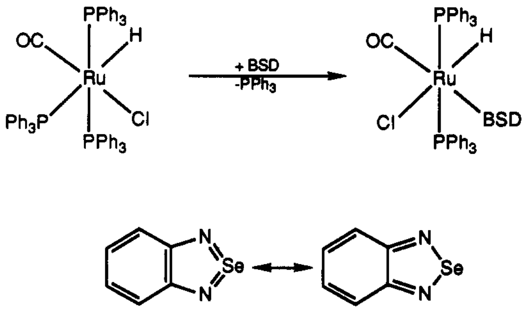
Received January 22, 1991

The reactions of [RuClH(CO)(BSD)(PPh$_3$)$_2$] (BSD = benzo-2,1,3-selenadiazole) with alkynes have been investigated and found to proceed readily with *cis*-hydroruthenation of the alkyne: The alkynes H—C$\equiv$C—R (R = H, ^{n}C$_4$H$_9$, C$_6$H$_4$Me-4, CMe$_2$OH) provide simple 18-electron σ-*E*-vinyl complexes [Ru(CH$=$CHR)Cl(CO)(BSD)(PPh$_3$)$_2$]; diphenylbutadiyne provides an α-(ethynyl)vinyl derivative [Ru{C(C$\equiv$CPh)$=$CHPh}Cl(CO)(BSD)(PPh$_3$)$_2$], whilst the propargylic ylide precursor HC$\equiv$C—CH$_2$CH(CO$_2$Et)PO(OEt)$_2$ yields the novel complex [Ru(CH$=$CH—CH$_2$CH(CO$_2$Et)PO(OEt)$_2$)Cl(CO)(BSD)(PPh$_3$)$_2$]. The BSD ligand in these complexes inhibits secondary insertion reactions but is sufficiently labile to be readily replaced by (2,6-dimethylphenyl)isonitrile to provide [Ru(vinyl)Cl(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$].

Introduction

Whilst acyclic sulfur diimides (diimino-λ^4-sulfuranes) are prone to rupture of the sulfur(IV) cumulene in reactions with transition-metal complexes and in particular metal hydrides, the complexes [RuClH(CO)(BTD)(PPh$_3$)$_2$] (BTD = benzo-2,1,3-thiadiazole) and [RuClH(CO)(BSD)(PPh$_3$)$_2$] (BSD = benzo-2,1,3-selenadiazole), prepared from the heterocycle and [RuClH(CO)(PPh$_3$)$_3$], are remarkably robust (Scheme I).[1] Nevertheless the heterocycle in these complexes is particularly labile and we therefore anticipate a rich chemistry. We describe herein the reactions of [RuClH(CO)(BSD)(PPh$_3$)$_2$] with a range of alkynes, which lead to hydroruthenation of the alkyne under very mild conditions and in high yield.

Scheme I



BSD = benzo-2,1,3-selenadiazole

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of prepurified dinitrogen by using conventional Schlenk-tube techniques. Solvents were purified by distillation from an appropriate drying agent (ethers, paraffins, benzene and toluene from sodium/potassium alloy with benzophenone as indicator; halocarbons and acetonitrile from CaH$_2$). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker WH-400 or Perkin Elmer R34 NMR spectrometer and calibrated against internal Me$_4$Si (^{1}H) or external H$_3$PO$_4$ (^{31}P). The assistance of O. W. Howarth and the Warwick University NMR service are gratefully acknowledged. Infrared spectra were recorded by using a Perkin-Elmer 1720-X FT-IR spectrometer. FAB mass spectrometry was carried out with a Kratos MS80 mass spectrometer using nitrobenzyl alcohol as matrix. Petroleum ether refers to that fraction of bp 40–60 °C. Data for the new complexes are given in Table I. The complex [RuClH(CO)(BSD)(PPh$_3$)$_2$][1] has been described elsewhere. Data for the complexes are collected in Table I. Attempts to obtain satisfactory elemental microanalytical data have been unsuccessful. Slow recrystallization of the complexes leads to loss of the BSD ligand, and recrystallization in the presence of excess BSD leads to cocrystallization of the ligand. Data given are for samples recrystallized in the presence of excess BSD and are consistently low in carbon: C$_6$H$_4$N$_2$Se requires 39.4% C.

Synthesis of [Ru(CH$=$CHC$_4$H$_9$)Cl(CO)(BSD)(PPh$_3$)$_2$]. A suspension of [RuClH(CO)(BSD)(PPh$_3$)$_2$] (0.20 g, 0.23 mmol) in dichloromethane (10 mL) was treated with hex-1-yne (0.1 g, excess) and the mixture heated to reflux to dissolve the complex. The solution was left to cool, stirred at room temperature for 10 h, and then diluted with methanol (25 mL) and left to stand for 30 min. Bright red needles of the title complex formed and were isolated by filtration, washed with diethyl ether (2 × 10 mL), and dried in vacuo. Yield: 0.19 g (87%). Anal. Calcd for C$_{49}$H$_{45}$ClON$_2$P$_2$RuSe: C, 61.6; H, 4.8; N, 2.9. Found: C, 57.6; H, 4.4; N, 2.9.

Synthesis of [Ru(CH$=$CHC$_6$H$_4$Me-4)Cl(CO)(BSD)(PPh$_3$)$_2$]. A suspension of [RuClH(CO)(BSD)(PPh$_3$)$_2$] (0.20 g, 0.23 mmol) in dichloromethane (10 mL) was treated with 4-

---

(1) Alcock, N. W.; Hill, A. F.; Roe, M. S. *J. Chem. Soc., Dalton Trans.* **1990**, 1737 and references therein.

(2) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1986**, *306*, 169. Torres, M. R.; Santos, A.; Ros, J.; Solans, X. *Organometallics* **1987**, *6*, 1901. Romero, A.; Santos, A.; Vegas, A. *Organometallics* **1988**, *7*, 1988. Romero, A.; Santos, A.; Lopez, J.; Eschavarren, A. M. *J. Organomet. Chem.* **1990**, *391*, 219. Torres, M. R.; Santos, A.; Perales, A.; Ros, J. *J. Organomet. Chem.* **1988**, *353*, 221.

0276-7333/91/2310-3903$02.50/0