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≡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

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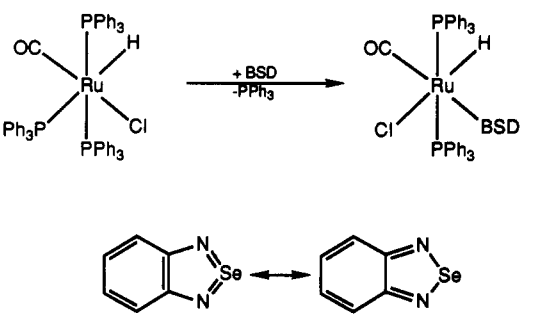
The reactions of [RuClH(CO)(BSD)(PPh_3)$_2$] (BSD = benzo-2,1,3-selenadiazole) with alkynes have been investigated and found to proceed readily with *cis*-hydroruthenation of the alkyne: The alkynes H—C≡C—R (R = H, $^nC_4H_9$, C_6H_4Me-4, CMe_2OH) provide simple 18-electron σ-*E*-vinyl complexes [Ru(CH=CHR)Cl(CO)(BSD)(PPh_3)$_2$]; diphenylbutadiyne provides an α-(ethynyl)vinyl derivative [Ru{C(C≡CPh)=CHPh}Cl(CO)(BSD)(PPh_3)$_2$], whilst the propargylic ylide precursor HC≡C—CH_2CH(CO_2Et)PO(OEt)$_2$ yields the novel complex [Ru(CH=CH—CH_2CH(CO_2Et)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)($CNC_6H_3Me_2$-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_4Si (^{1}H) or external H_3PO_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: $C_6H_4N_2Se$ requires 39.4% C.

Synthesis of [Ru(CH=CHC_4H_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 $C_{49}H_{45}ClON_2P_2RuSe$: C, 61.6; H, 4.8; N, 2.9. Found: C, 57.6; H, 4.4; N, 2.9.

Synthesis of [Ru(CH=CHC_6H_4Me-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.

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Table I. Spectroscopic Data for the Complexes [Ru(CHCHR)Cl(CO)(PPh_3)$_2$] and [Ru($C_4HR'_2$)Cl(CO)(PPh_3)$_2$]

	infrared[a]		NMR[b]	
	ν(CO)	other	^{31}P	^{1}H
R = H (gold)	1926 (1928)	1556 (m), 1515 (m), 1313 (w), 1289 (m), 886 (m)	26.25	4.89 [d × d, 1 H, $RuCH_a{=}CH_bH_c$ (H_c cis to Ru), $J(H_aH_c)$ 17.7, $J(H_bH_c)$ ca. 1.5 Hz], 5.67 [d × d, 1 H, $RuCH_a{=}CH_aH_c$ (H_b trans to Ru, $J(H_aH_b)$ 9.9, $J(H_bH_c)$ ca. 1.5 Hz], 7.04–7.60 [m × 7, 34 H, C_6H_5 and C_6H_4], 8.18 [d × d × t, 1 H, $P_2RuCH_a{=}CH_bH_c$, $J(P_2H_a)$ 3.2, $J(H_aH_b)$ 9.9, $J(H_aH_c)$ 17.6 Hz]
R = C_5H_{11} (red)	1936 (1924)	1573 (w), 1287 (w), 1252 (w), 1220 (w)	26.39	0.72 [t, 3 H, $Ru(CH)_2(CH_2)_3CH_3$, J(HH) 6.9 Hz], 0.86–1.31 [m, 4 H, $Ru(CH)_2(CH_2)(CH_2)_2CH_3$], 1.85, 1.87, 1.88, 1.90 [m (br), 2 H, $Ru(CH)_2(CH_2)(CH_2)_2CH_3$], 4.86, 4.87, 4.89, 4.91, 4.93 [m (br), 1 H, $RuCH{=}CHC_4H_9$], 5.28 [s, 1 H, CH_2Cl_2 hemisolvate], 7.05–7.70 [m × 5, 34 H, C_6H_5 and C_6H_4], 7.91 [s (v br), 1 H, $RuCH{=}CHC_4H_9$]
R = C_6H_4Me (red)	1918 (1913)	1574 (m), 1546 (m), 1507 (m), 1287 (w), 1265 (w), 1220 (w)	26.53	2.26 [s, 3 H, $C_6H_4CH_3$], 5.28 [s, 1 H, CH_2Cl_2 hemisolvate], 5.78 [d, 1 H, $RuCH{=}CHC_6H_4CH_3$, J(HH) 16.7 Hz], 6.77, 6.93 [(AB)$_2$, 4 H, $RuCH{=}CHC_6H_4CH_3$, J(AB) 8.0 Hz], 7.04–7.96 [m × 8, 34 H, C_6H_4 and C_6H_5], 8.64 [d × t, 1 H, $P_2RuCH{=}CHC_6H_4CH_3$, $J(P_2H)$ 3.1 Hz]
R = CMe_2OH (orange)	1921 (1927)	1587 (w), 1284 (w), 1242 (w), 1162 (m), 1075 (s), 845 (m)	26.30, 24.43	0.82 [s, 6 H, $RuCHCHC(CH_3)OH$], 3.46 [s (br), 1 H, $RuCHCHC(CH_3)OH$,], 5.49 [d × t, 1 H, $P_2RuCHCH(CH_3)OH$, $J(P_2H)$ 1.9, J(HH) 16.7 Hz], 7.04–7.6 [m × 5, 34 H, C_6H_4 and C_6H_5], 7.66 [d × t, 1 H, $P_2RuCHCHC(CH_3)OH$, $J(P_2H)$ 3.1, J(HH) 16.8 Hz]
R = $CH_2CH(CO_2Et)$-$PO(OEt)_2$ (yellow)	1919 (1927)	1720 (s), 1587 (w), 1318 (w), 1298 (w), 1246 (s), 1158 (m), 1017 (s), 967 (s), 869 (w), 855 (w)	26.34, 26.16,[c] 24.24[d]	1.05 [t, 3 H, $COCH_2CH_3$, J(HH) 7.1 Hz], 1.29 [d × t, 6 H, $POCH_2CH_3$, J(PH) ≅ J(HH) 5.3 Hz], 2.53 [t × d, 1 H, $CH_2CH(CO_2Et)$-$PO(OEt)_2$], 3.47 [q, 2 H, $CO_2CH_2CH_3$, J(HH) 7.0 Hz], 3.76 [ABXY, 2 H, $RuCH{=}CHCH_2CHP$, J(AB) 5.3, J(AX) 10.8 Hz], 4.04, 4.08 [q × 2, 4 H, $P(OCH_2CH_3)_2$, J(HH) 7.3 Hz], 4.88 [d × t (br), 1 H, $RuCH_aCH_bCH_c$, $J(H_aH_b)$ 15.6 Hz, $J(H_bH_c)$ not resolved], 7.06–7.69 [m × 6, 34 H C_6H_4 and C_6H_5], 7.90 [s (v br), 1 H, $RuCHCHCH_2$]
R′ = C_6H_5 (purple)	1912 (1927)	1596 (m), 1519 (w), 1290 (w), 1269 (w), 914 (w)	27.97	6.59 [s (br), 1 H, $C{=}CHPh$], 6.91–7.81 [m × 5, 44 H, C_6H_5 and C_6H_4]

[a] Data from Nujol mulls, values given in parentheses from dichloromethane solution. [b] Data from saturated solutions in $CDCl_3$, given in ppm relative to internal $SiMe_4$ (^{1}H) or external H_3PO_4 (^{31}P). [c] Resonance due to $PO(OEt)_2$. [d] Outer pair of resonances for AB quartet not observed.

ethynyltoluene (0.05 g, excess). The mixture was stirred at room temperature for 1 h and then diluted with methanol (25 mL) and left to stand for 30 min. Red microcrystals of the title complex formed and were isolated by filtration, washed with diethyl ether (2 × 10 mL), and dried in vacuo. Yield: 0.20 g (88%). Anal. Calcd for $C_{52}H_{43}ClON_2P_2RuSe$: C, 63.1; H, 4.4; N, 2.8. Found: C, 62.0; H, 4.3; N, 2.8.

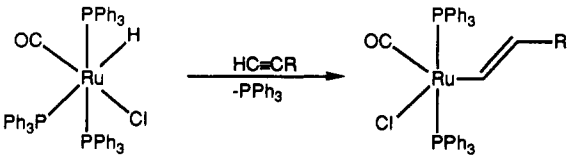
Synthesis of [Ru(CH=CH_2)Cl(CO)(BSD)(PPh_3)$_2$]. A stream of acetylene was passed through a solution of [RuClH(CO)(BSD)(PPh_3)$_2$] (0.20 g, 0.23 mmol) in dichloromethane (25 mL) for 1 min. The vessel was sealed and the mixture stirred for 5 h. The solution was concentrated under reduced pressure to ca. 10 mL, diluted with methanol (20 mL), and cooled to −10 °C overnight. The gold/brown needles which formed were isolated by filtration, washed with diethyl ether (2 × 10 mL), and dried in vacuo. Yield: 0.12 g (58%).

Synthesis of [Ru(CH=$CHCMe_2OH$)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 3,3-dimethyl-prop-1-yn-3-ol (0.2 g, excess). The mixture was stirred at room temperature for 10 h and then heated under reflux for 5 min. The solution was left to cool, diluted with methanol (25 mL), and left to stand for 30 min. Fine orange needles of the title complex formed and were isolated by filtration, washed with diethyl ether (2 × 10 mL), and dried in vacuo. Yield: 0.17 g (77%).

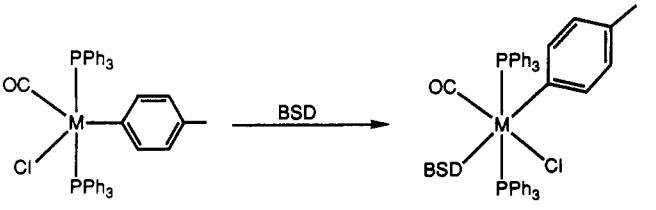
Synthesis of [Ru{C(C≡CC_6H_5)=CHC_6H_5}Cl(CO)(BSD)(PPh_3)$_2$]. A suspension of [RuClH(CO)(BSD)(PPh_3)$_2$] (0.20 g, 0.23 mmol) in dichloromethane (10 mL) was treated with diphenylbutadiyne (0.05 g, 0.26 mmol). The mixture was stirred at room temperature for 10 h and then heated under reflux for 5 min. The solution was left to cool, diluted with methanol (25 mL), and left to stand for 30 min. Purple needles of the title complex formed and were isolated by filtration, washed with diethyl ether (2 × 10 mL), and dried in vacuo. Yield: 0.18 g (72%). The complex was characterized by comparison of spectroscopic data with those of an authentic sample prepared according to ref 3. Anal. Calcd for $C_{59}H_{45}ClN_2OP_2RuSe$: C, 65.9; H, 4.2; N, 2.6. Found: C, 63.2; H, 4.0; N, 2.5.

Synthesis of [Ru{CH=$CHCH_2CH(CO_2Et)PO(OEt)_2$}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 triethyl α-propargylphosphonoacetate (0.058 g, 0.30 mmol). The mixture was stirred at room temperature for 10 h and then heated under reflux for 5 min. The solution was left to cool, diluted with methanol (25 mL), and concentrated under reduced pressure (rotary evaporator) to ca. 10 mL. The yellow microcrystalline solid thus formed was isolated by filtration, washed with diethyl ether (2 × 10 mL), and dried in vacuo. Yield: 0.14 g (69%). Anal. Calcd for $C_{54}H_{56}ClO_6N_2P_3RuSe$: C, 57.0; H, 5.0; N, 2.5. Found: C, 55.0; H, 4.7; N, 2.5.

Scheme II



Scheme III



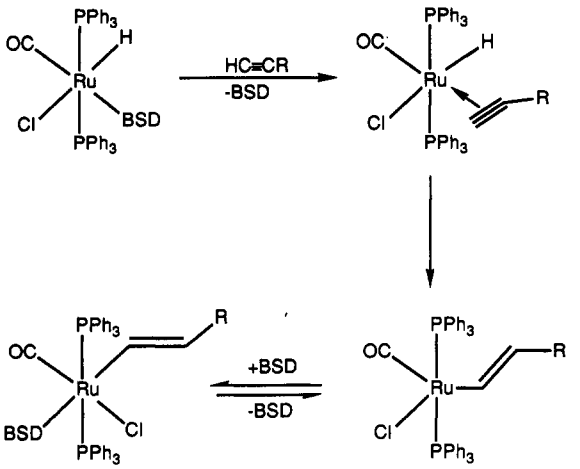
M = Ru, Os

Results and Discussion

Santos and co-workers have recently described the hydroruthenation of a range of simple alkynes by the complex [RuClH(CO)(PPh_3)$_3$], a reaction which proceeds under mild conditions (Scheme II).[2] Similar reactions ensue with the complexes [RuClH(CO)(PPh_3)$_2$(L)] (L = pyridine, 3,5-dimethylpyrazole); however the products retain the heterocycles.[2] We have been concerned with the extension of this reaction to other more exotic alkynes including 1,3-diynes[3] and propargylphosphonium salts.[4] The

(3) Hill, A. F.; Melling, R. P. *J. Organomet. Chem.* **1990**, *396*, C22. Hill, A. F.; Melling, R. P.; Thompsett, A. R. Manuscript in preparation.

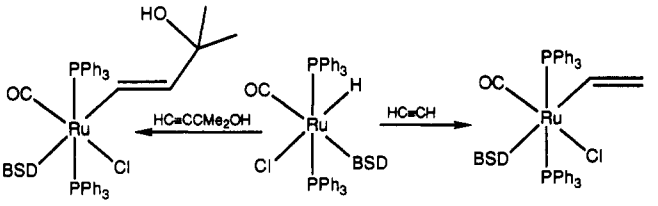
Scheme IV



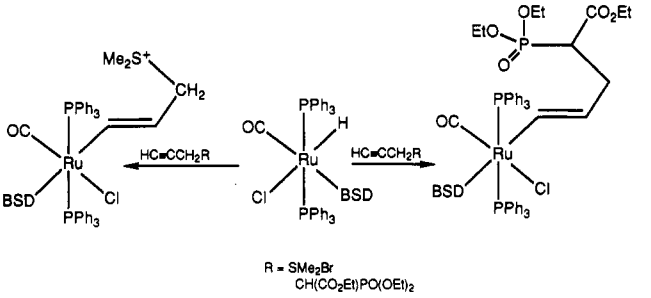
products of these reactions are 16-electron species, and a simple color test of coordinative unsaturation, which we have had recourse to in these studies, is the reaction of complexes with benzo-2,1,3-selenadiazole, since the 18-electron adducts formed are invariably brightly colored. Thus, e.g., the σ-aryl complexes [M(C$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$] (M = Ru, Os[5]) react rapidly with BSD to provide the adducts [M(C$_6$H$_4$Me-4)Cl(CO)(BSD)(PPh$_3$)$_2$] (Scheme III).[6] The hydrido complex [RuClH(CO)(PPh$_3$)$_3$] itself reacts with BSD to provide the intensely colored yellow/brown complex [RuClH(CO)(BSD)(PPh$_3$)$_2$] due to the lability of one phosphine ligand in the tris(phosphine) complex. In the case of the complexes [M(C$_6$H$_4$Me-4)Cl(CO)(BSD)(PPh$_3$)$_2$], treatment with carbon monoxide provided the dicarbonyl derivatives [M(C$_6$H$_4$Me-4)Cl(CO)$_2$(PPh$_3$)$_2$] by substitution of the heterocycle, indicating its lability.[6] We therefore expected that the hydrido complex [RuClH(CO)(BSD)(PPh$_3$)$_2$] might serve as a convenient, air-stable source of the "[RuClH(CO)(PPh$_3$)$_2$]" fragment for hydroruthenation studies.

A solution of [RuClH(CO)(BSD)(PPh$_3$)$_2$] in dichloromethane reacts with 4-ethynyltoluene to provide a deep red compound of formulation [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BSD)(PPh$_3$)$_2$] in high yield. This complex is also accessible via the reaction of preformed [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$] with BSD, and the former is presumably an intermediate in the reaction of [RuClH(CO)(BSD)(PPh$_3$)$_2$] with HC≡CC$_6$H$_4$Me-4 (Scheme IV). A similar though somewhat slower reaction ensues between [RuClH(CO)(BSD)(PPh$_3$)$_2$] and 1-hexyne, to provide bright red needles of [Ru(CH=CHC$_4$H$_9$)Cl(CO)(BSD)(PPh$_3$)$_2$] upon addition of methanol. On the basis of the assumption that the 16-electron σ-vinyl complexes [Ru(CH=CHR)Cl(CO)(PPh$_3$)$_2$] (R = C$_6$H$_4$Me-4, C$_5$H$_9$) are intermediates in the formation of [Ru(CH=CHR)Cl(CO)(BSD)(PPh$_3$)$_2$] and indeed in equilibrium with the latter, we assume that the stereochemistry of the complexes involves a mutually trans disposition of phosphines and coordination of the heterocycle trans to the σ-vinyl ligand. This site of addition to the 16-electron precursors appears to be that found in the kinetic product of addition of ligands to complexes of the general form [RuClR(CO)(PPh$_3$)$_2$], as shown by Roper for isonitriles,[7] ourselves

Scheme V

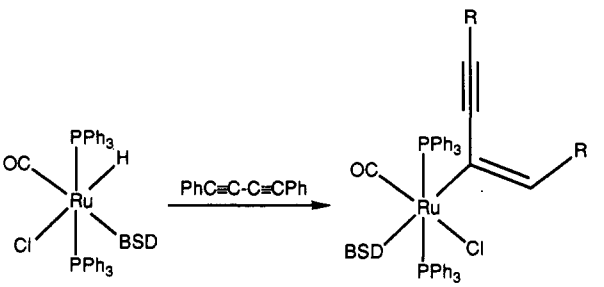


Scheme VI



R = SMe$_2$Br
CH(CO$_2$Et)PO(OEt)$_2$

Scheme VII



for the crystallographically characterized complex [Os(C$_6$H$_4$Me-4)Cl(CO)(SNNMe$_2$)(PPh$_3$)$_2$],[8] Werner for the compounds [M(CH=CHR)Cl(CO)(PR′R″$_2$)$_2$],[9] and Santos and co-workers for [Ru(CH=CHR)Cl(CO)(PPh$_3$)$_2$].[2]

The parent complex for the series [Ru(CH=CH$_2$)Cl(CO)(BSD)(PPh$_3$)$_2$] forms readily upon passing a stream of ethyne through a solution of [RuClH(CO)(BSD)(PPh$_3$)$_2$] in dichloromethane. The complex was isolated in modest yield, and no attempt was made to maximize the yield. In contrast, the reaction of [RuClH(CO)(PPh$_3$)$_3$] with ethyne proceeds with considerable secondary insertion of further alkyne to provide mixtures of polyenyl species unless care is taken to keep the concentration of ethyne low.[2]

Functionalized Alkynes. Following the isolation of simple hydrocarbyl-substituted alkynes, the extension of the reaction to functionalized alkynes was nest investigated: The propargylic alcohol HC≡CCMe$_2$OH reacts with [RuClH(CO)(BSD)(PPh$_3$)$_2$] to provide the orange γ-hydroxypropenyl derivative [Ru(CH=CHCMe$_2$OH)Cl(CO)(BSD)(PPh$_3$)$_2$] in high yield (Scheme V). The Wittig–Horner reagent HC≡CCH$_2$CH(CO$_2$Me)PO(OEt)$_2$ also undergoes *cis*-hydroruthenation with [RuClH(CO)(BSD)(PPh$_3$)$_2$] to provide the unusual complex [Ru{CH=CHCH$_2$CH(CO$_2$Et)PO(OEt)$_2$}Cl(CO)(BSD)(PPh$_3$)$_2$] (Scheme VI). This compound suggests the possibility of generating an ylidic site at a position δ to the metal center

(4) Alcock, N. W.; Hill, A. F.; Rawles, H. M. Submitted for publication in *Organometallics*.
(5) (a) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1. (b) Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *Ibid.* **1990**, *389*, 375. (c) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Ibid.* **1988**, *358*, 411.
(6) Herberhold, M.; Hill, A. F. *J. Organomet. Chem.* **1989**, *377*, 151.
(7) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1978**, *157*, C27.
(8) (a) Herberhold, M.; Hill, A. F. *J. Organomet. Chem.* **1986**, *315*, 105. (b) Gieren, A.; Ruiz-Perez, C.; Hübner, T.; Herberhold, M.; Hill, A. F. *J. Chem. Soc., Dalton Trans.* **1988**, 1693.
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upon treatment with a nonnucleophilic base, and we are currently investigating this chemistry.

Diynes. $[RuClH(CO)(PPh_3)_3]$ reacts with diphenylbutadiyne or bis(phenylethynyl)mercury to provide the α-phenylethynyl-*trans*-β-styryl complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$,[3] and part of our characterization of this complex involved its reaction with BSD to provide the purple complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(BSD)(PPh_3)_2]$. This compound is also the exclusive product of the reaction of $[RuClH(CO)(BSD)(PPh_3)_2]$ with diphenylbutadiyne (Scheme VII).

Reactions with Isonitriles. The reactions of $[M(C_6H_4Me\text{-}4)Cl(CO)(BSD)(PPh_3)_2]$ (M = Ru, Os) with carbon monoxide lead to rapid displacement of the heterocycle and formation of the dicarbonyl complexes $[M(C_6H_4Me\text{-}4)Cl(CO)_2(PPh_3)_2]$.[6] In a similar reaction, we find that the vinyl complexes described above react rapidly with 1 equiv of (2,6-dimethylphenyl)isonitrile to liberate the heterocycle with formation of the isonitrile complex $[Ru(vinyl)Cl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$. The reactions of $[Ru(CH{=}CHR)Cl(CO)(PPh_3)_2(L)]$ (L = pyridine, 3,5-dimethylpyrazole) with ^{t}BuNC also lead to replacement of the heterocycle.[10]

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Registry No. $[Ru(CH{=}CHC_4H_9)Cl(CO)(BSD)(PPh_3)_2]$, 136570-77-9; $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BSD)(PPh_3)_2]$, 136570-78-0; $[Ru(CH{=}CH_2)Cl(CO)(BSD)(PPh_3)_2]$, 136570-79-1; $[Ru(CH{=}CHCMe_2OH)Cl(CO)(BSD)(PPh_3)_2]$, 136570-80-4; $[Ru\{C(C{\equiv}CC_6H_5){=}CHC_6H_5\}Cl(CO)(BSD)(PPh_3)_2]$, 136570-81-5; $[Ru\{CH{=}CHCH_2CH(CO_2Et)PO(OEt)_2\}Cl(CO)(BSD)(PPh_3)_2]$, 136570-82-6; $[RuClH(CO)(BSD)(PPh_3)_2]$, 128817-72-1; $HC{\equiv}CC_6H_4Me\text{-}4$, 766-97-2; $HC{\equiv}CC_4H_9$, 693-02-7; $HC{\equiv}CH$, 74-86-2; $HC{\equiv}CMe_2OH$, 115-19-5; $C_6H_5C{\equiv}CC{\equiv}CC_6H_5$, 886-66-8; $HC{\equiv}CCH_2CH(CO_2Et)PO(OEt)_2$, 26199-74-6; $CNC_6H_3Me_2\text{-}2,6$, 2769-71-3.

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Bond-Forming Reactions to a Coordinated Hydroxo Group: Reaction of *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ with MeI, EtI, HCl, $CH_3C(O)Cl$, and H_2

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Reactions of *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ with MeI, EtI, HCl, and $CH_3C(O)Cl$ lead to the formation of bonds between the hydroxide and the adding group. For MeI and EtI addition, where the alcohols are formed, the reactions occur by oxidative addition followed by reductive elimination to form the carbon–oxygen bond. Reaction with HCl proceeds very rapidly by protonation of the hydroxide to eliminate H_2O. The reaction of *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ with acetyl chloride gives a mixture of products from initial attack of acetyl chloride on the hydroxide to produce acetic acid. Subsequent oxidative addition of the acid produces an acetate complex. Reaction of *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ with H_2 produces the trihydride $H_3Ir(CO)(P(p\text{-tolyl})_3)_2$ and H_2O. This reaction is partially reversible; treatment of the trihydride with H_2O produces the hydroxy complex. The reactions reported here are among the first that exhibit bond formation to a metal-bound hydroxo group.

Hydroxide complexes are central to catalytic reactions such as the Wacker process[1] and water–gas shift reactions.[2] Despite this importance relatively few hydroxide complexes of low oxidation state transition metals have been prepared.[3] One synthetic route to hydroxide complexes involves hydrolysis of alkoxide complexes.[4,5]

$$Pt(CCl{=}CCl_2)(OMe)(PPh_3)_2 + H_2O \rightarrow Pt(CCl{=}CCl_2)(OH)(PPh_3)_2 + MeOH \quad (1)$$

$$Ir(CO)(OMe)(PPh_3)_2 + H_2O \rightarrow Ir(CO)(OH)(PPh_3)_2 + MeOH \quad (2)$$

A second route involves displacement of coordinated solvent with hydroxide.[6,7]

$$Pt(Cl)(Me)L_2 \xrightarrow[\text{acetone}]{AgBF_4} [Pt(\text{acetone})(Me)L_2^+] \xrightarrow{KOH} Pt(OH)(Me)L_2 \quad (3)$$

L = a tertiary phosphine

$$Ir(CO)(CH_3CN)(PPh_3)_2^+ + OH^- \rightarrow Ir(CO)(OH)(PPh_3)_2 + CH_3CN \quad (4)$$

Reactivity studies of such hydroxide complexes have been limited to reactions with weak acids to eliminate H_2O[4,6-8]

$$Pt(OH)(Me)L_2 + HX \rightarrow Pt(X)(Me)L_2 + H_2O \quad (5)$$

L = a tertiary phosphine, X = $CH_2C(O)CH_3$, CH_2NO_2, etc.

and reaction with CO forming a carboxylic acid that may decompose to a hydride and CO_2.[9,10]

$$Pt(OH)(Ph)(PEt_3)_2 + CO \rightarrow Pt(CO_2H)(Ph)(PEt_3)_2 \quad (6)$$

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