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Diyne Coordination Chemistry. 4. Synthesis, Molecular Structure, and Protonation Reactions of the Zerovalent Complex $[Ru(\eta^2\text{-}PhC{\equiv}C{-}C{\equiv}CPh)(CO)_2(PPh_3)_2]$[1]

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The reaction of $[Ru(CO)_2(PPh_3)_3]$ with diphenylbutadiyne provides the complex $[Ru(\eta^2\text{-}PhC{\equiv}C{-}C{\equiv}CPh)(CO)_2(PPh_3)_2]$ (**1**) which in turn reacts with Brønsted acids, protonation occurring at a coordinated carbon to give 1,4-diphenylbut-1-en-3-yn-2-ylruthenium(II) complexes. Thus $[Ru(\eta^2\text{-}PhC{\equiv}C{-}C{\equiv}CPh)(CO)_2(PPh_3)_2]$ with HPF_6 and HCl gives the complexes $[Ru(\eta^3\text{-}PhC{\equiv}C{-}C{=}CHPh)(CO)_2(PPh_3)_2]^+$ (**2**$^+$) and $[Ru(\eta^1\text{-}PhC{\equiv}C{-}C{=}CHPh)Cl(CO)_2(PPh_3)_2]$ (**3**), respectively, the latter being also the product of the reaction of the former with chloride ion or of the hydridoruthenium complex $[RuClH(CO)(PPh_3)_3]$ with diphenylbutadiyne followed by carbon monoxide. The salt $[Ru(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)(CO)_2(PPh_3)_2]PF_6$ (**2**·PF_6) was characterized crystallographically [crystals are triclinic of space group P_1, $Z = 4$, in a unit cell of dimensions $a = 16.750$ (8) Å, $b = 17.280$ (9) Å, $c = 20.297$ (10) Å, $\alpha = 96.10$ (4)°, $\beta = 111.50$ (4)°, $\gamma = 106.29$ (4)°, $U = 5101$ (4) Å^3], confirming the *trihapto* coordination which subsequent chemistry, however, indicates is *hemilabile*. The salt reacts with neutral 2-electron ligands acetonitrile, *tert*-butylisonitrile, and 2,6-dimethylphenyl isocyanide to afford the *monohapto*, 1,4-diphenylbut-1-en-3-yn-2-yl derivatives $[Ru(\eta^1\text{-}C(C{\equiv}CPh){=}CHPh)(CO)_2(L)(PPh_3)_2]PF_6$ (L = NCMe (**4a**·PF_6), CN^tBu (**4b**·PF_6), $CNC_6H_3Me_2$-2,6 (**4c**·PF_6)), the acetonitrile ligation in **4a**·PF_6 being reversible. The neutral azido derivative $[Ru\{\eta^1\text{-}C(C{\equiv}CPh){=}CHPh\}N_3(CO)_2(PPh_3)_2]$ (**5**) results from reaction of **2**·PF_6 with sodium azide. Complexes **3** and **2**$^+$ react with excess hydrochloric acid to cleave the vinyl ligand and provide $[RuCl_2(CO)_2(PPh_3)_2]$.

Introduction

The coordinative activation of alkynes toward chemical modification provides the basis of transition-metal-mediated hydrogenation,[2] hydrosilation,[3] and hydrocyanation.[4] The important stage in these processes following alkyne coordination is the transfer of a hydrogen to the alkyne. We have been concerned with the interaction of metal hydrides with 1,3-diynes which leads intramolecularly to the formation of 1-en-3-yn-2-yl ligands.[1,5,6] This report describes the synthesis of a 1,3-diyne complex of zerovalent ruthenium and its *inter*molecular proton-transfer reactions with Brønsted acids to provide an alternative entry into the chemistry of 1-en-3-yn-2-yl ligands. A preliminary report of aspects of this work has appeared.[5]

Experimental Section

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

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WH-400, Perkin-Elmer R34 NMR, or JEOL JNM-EX270 spectrometer and calibrated against internal Me_4Si (^1H) or external H_3PO_4 (^{31}P). Infrared spectra were recorded 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 Tables IV and V. The complexes $[RuCl\{C(C{\equiv}CPh){=}CHPh\}(CO)(PPh_3)_2]$[5] and $[Ru(CO)_2(PPh_3)_3]$[7] have been described elsewhere.

Synthesis of $[Ru(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(CO)_2(PPh_3)_2]$ (1). A suspension of $[Ru(CO)_2(PPh_3)_3]$ (1.00 g, 1.06 mmol) in tetrahydrofuran (10 cm^3) was treated with diphenylbutadiyne (0.22 g, 1.08 mmol) and the mixture stirred for 20 min. Ethanol (30 cm^3) was added to complete precipitation of the crude alkyne complex which was isolated by filtration and washed successively with ethanol (10 cm^3) and petroleum ether (2 × 10 cm^3) to remove phosphine. The bright yellow residue was chromatographed on silica gel eluting with dichloromethane as the only bright yellow band. The solvent was removed from the eluate and the residue crystallized from dichloromethane/ethanol. Yield: 0.89 g (95%). FAB-MS: 884 $[M]^+$, 595 $[M - CO - PPh_3]^+$, 567 $[M - 2CO - PPh_3]^+$, 487 $[RuPPh_3(C_4HPh)]^+$, 393 $[Ru(CO)PPh_3]^+$, 363 $[RuPPh_3]^+$.

Synthesis of $[Ru(\eta^3\text{-}PhCCCCHPh)(CO)_2(PPh_3)_2]PF_6$ (2·PF_6). A solution of $[Ru(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(CO)_2(PPh_3)_2]$ (1) (0.50 g, 0.56 mmol) in dichloromethane (30 cm^3) was treated with a solution of concentrated hexafluorophosphoric acid (2 drops) in ethanol (10 cm^3) and the mixture stirred for 10 min. Further

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ethanol was added as necessary to maintain solution homogeneity. The solvent mixture was concentrated under reduced pressure to effect formation of pale yellow crystals of the salt which were isolated by filtration and, if necessary, recrystallized from dichloromethane/toluene. Yield: 0.40 g (69%). FAB-MS ($\mathbf{2}\cdot BF_4$): 885 $[M]^+$, 857 $[M - CO]^+$, 623 $[Ru(PPh_3)_2]^+$, 595 $[M - PPh_3 - CO]^+$, 489 $[RuPPh_3(C_4HPh)]^+$, 363 $[RuPPh_3]^+$.

Synthesis of $[Ru\{\eta^1\text{-}C(C{\equiv}CPh){=}CHPh\}Cl(CO)_2(PPh_3)_2]$ (3). A stream of carbon monoxide was passed through a solution of $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$ (0.20 g, 0.22 mmol) in dichloromethane (15 cm^3). The solution was stirred for 10 min during which time it decolorized to a pale yellow. Ethanol (20 cm^3) was added and the total solvent volume slowly reduced in vacuo to ca. 10 cm^3 to effect formation of pale yellow crystals of the product which were isolated by filtration, washed with ethanol (10 cm^3) and diethyl ether (10 cm^3), and dried in vacuo. Yield: quantitative. FAB-MS: 885 $[M - Cl]^+$, 857 $[M - Cl - CO]^+$, 689 $[RuCl(CO)(PPh_3)_2]^+$, 625 $[Ru(PPh_3)_2]^+$, 595 $[RuPPh_3(CO)(C_4HPh_2)]^+$, 489 $[RuPPh_3(C_4HPh)]^+$, 363 $[RuPPh_3]^+$.

Synthesis of $[Ru\{\eta^1\text{-}C(C{\equiv}CPh){=}CHPh\}N_3(CO)_2(PPh_3)_2]$ (5). A suspension of $\mathbf{2}\cdot PF_6$ (0.20 g, 0.19 mmol) and sodium azide (0.03 g, 2 equiv) in ethanol (10 cm^3) was stirred for 8 h. The pale yellow precipitate which formed was isolated by filtration, washed with ethanol (10 cm^3), and dried in vacuo. Yield: 0.12 g (68%). FAB-MS: 885 $[M - N_3]^+$, 626 $[Ru(PPh_3)_2]^+$, 566 $[RuPPh_3(C_4HPh_2)]^+$, 489 $[RuPPh_3(C_4HPh)]^+$.

Synthesis of $[Ru(\eta^1\text{-}PhCCCCHPh)(CO)_2(NCMe)(PPh_3)_2]PF_6$ ($\mathbf{4a}\cdot PF_6$). A solution of $[Ru(\eta^3\text{-}PhCCCCHPh)(CO)_2(PPh_3)_2]PF_6$ ($\mathbf{2}\cdot PF_6$) (0.20 g, 0.19 mmol) in acetonitrile (5 cm^3) was treated with petroleum ether (30 cm^3) to effect precipitation of the acetonitrile adduct which was isolated by filtration. Attempts to recrystallize this complex in the absence of acetonitrile led to substantial loss of the coordinated nitrile. Yield: 0.18 g (88%). FAB-MS: 886 $[M - NCMe]^+$, 858 $[M - CO - NCMe]^+$, 654 $[Ru(CO)(PPh_3)_2]^+$, 623 $[Ru(PPh_3)_2]^+$, 595 $[RuPPh_3(CO)C_4HPh_2]^+$, 567 $[RuPPh_3(C_4HPh_2)]^+$, 489 $[RuPPh_3(C_4HPh)]^+$.

Synthesis of $[Ru(\eta^1\text{-}PhCCCCHPh)(CO)_2(CN^tBu)(PPh_3)_2]PF_6$ ($\mathbf{4b}\cdot PF_6$). A solution of $[Ru(\eta^3\text{-}PhCCCCHPh)(CO)_2(PPh_3)_2]PF_6$ ($\mathbf{2}\cdot PF_6$) (0.20 g, 0.20 mmol) in dichloromethane (10 cm^3) was treated with *tert*-butyl isocyanide and the mixture stirred for 10 min. Ethanol (20 cm^3) was added and the solvent volume reduced in vacuo to ca. 10 cm^3, and the yellow crystals were isolated by filtration and washed with petroleum ether (2 × 10 cm^3). Yield: 0.12 g (56%). FAB-MS ($\mathbf{4b}\cdot ClO_4$): 969 $[M]^+$, 941 $[M - CO]^+$, 885 $[M - CN^tBu]^+$, 678 $[M - CO - PPh_3]^+$, 650 $[M - 2CO - PPh_3]^+$.

The complex $[Ru(\eta^1\text{-}PhCCCCHPh)(CO)_2(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]PF_6$ ($\mathbf{4c}\cdot PF_6$) was prepared in an analogous manner and in comparable yields. FAB-MS ($\mathbf{4c}\cdot ClO_4$): 1016 $[M]^+$, 989 $[M - CO]^+$, 961 $[M - 2(CO)]^+$, 754 $[M - PPh_3]^+$, 726 $[M - CO - PPh_3]^+$, 698 $[M - 2(CO) - PPh_3]^+$, 566 $[RuPPh_3(C_4HPh_2)]^+$, 489 $[RuPPh_3(C_4HPh)]^+$, 363 $[RuPPh_3]^+$.

Structure Determination of $[Ru(\eta^3\text{-}PhCCCCHPh(CO)_2(PPh_3)_2]PF_6$. Crystal Data, X-ray Data Collection, and Structural Determination. Yellow prisms of the title salt ($\mathbf{2}\cdot PF_6$) were grown by diffusion of hexane into a dichloromethane solution of the crude material. That chosen for data collection (ca. 0.13 × 0.21 × 0.31 mm) was mounted on a glass fiber: Diffracted intensities were collected (θ–2θ scans) at 298 K in the range $3° < 2\theta < 50°$, on a Nicolet P3m four-circle diffractometer. Of 13 358 unique reflections, 8325 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, the latter by the Gaussian method based on complete definition of crystal morphology (transmission factors: max, 0.94; min, 0.89).

Crystal Data for $[Ru(\eta^3\text{-}PhCCCCHPh)(CO)_2(PPh_3)_2]PF_6$ ($\mathbf{2}\cdot PF_6$): $C_{56}H_{41}F_6O_2P_3Ru$, $M = 1053.93$, triclinic, $a = 16.750$ (8) Å, $b = 17.280$ (9) Å, $c = 20.297$ (10) Å, $\alpha = 96.10$ (4)°, $\beta = 111.50$ (4)°, $\gamma = 106.29$ (4)°, $U = 5101$ (4) Å^3, $Z = 4$, $D_c = 1.37$ g cm^{-3}, $F(000) = 2232$, space group $P\bar{1}$, Mo Kα X radiation ($\lambda = 0.710\,73$ Å, graphite monochromator), μ(Mo Kα) = 0.51 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 hydrogen atoms were included in calculated positions (C–H, 0.96 Å) with fixed isotropic thermal parameters. All non-hydrogen atoms were refined anisotropically (blocked least-squares; 685 parameters), with the exception of phenyl ring carbons and the hexafluorophosphate counteranions which were refined as rigid groups. The refinement converted at $R = 0.058$ ($R_w = 0.059$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0010|F|^2]$. The only residual electron-density peaks on the final difference synthesis were between −0.56 and 0.63 e Å^{-3}. Scattering factors and corrections for anomalous dispersion were taken from ref 8. All calculations were carried out using a DEC micro-Vax II computer with the SHELXTL PLUS suite of programs.[9] Selected bond lengths and angles and atomic coordinates are given in Tables I and II; thermal parameters and hydrogen atom positions have been deposited as supplementary material.

Results and Discussion

The complex $[Ru(CO)_2(PPh_3)_3]$ has been shown to react with diphenylacetylene via substitution of one labile phosphine ligand to provide the complex $[Ru(CO)_2(PPh_3)_2(Ph{-}C{\equiv}C{-}Ph)]$.[7] A similar reaction ensues when diphenylacetylene is replaced by diphenylbutadiyne (Scheme I). The resulting complex is bright yellow in contrast to the colorless mono-yne derivative. The complex may also be prepared via the reaction of $[RuH(NCMe)(CO)_2(PPh_3)_2]ClO_4$ with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of diphenylbutadiyne. Spectroscopic data (Tables IV and V) are consistent with the formulation of this complex as $[Ru(CO)_2(PPh_3)_2(Ph{-}C{\equiv}C{-}C{\equiv}C{-}Ph)]$. In addition to bands attributable to ν(CO) stretching, two bands of medium intensity are apparent at 2136 and 1742 cm^{-1}, which correspond to the ν(CC) absorption of the free and coordinated C≡C triple bonds. Similar frequencies (2170 and 1725 cm^{-1}) are observed for the free and coordinated alkyne groups in the complex $[Pt(PPh_3)_2(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)]$.[10]

The reaction of the alkyne complex $[Pt(PPh_3)_2(Ph{-}C{\equiv}C{-}Ph)]$ with excess hydrochloric acid leads to $[PtCl_2(PPh_3)_2]$[11] and stilbene and a reasonable intermediate in this reaction might be the σ-vinyl complex $[Pt(CPh{=}CHPh)Cl(PPh_3)_2]$. There has been considerable recent interest in the chemistry of α-alkynylvinyl ligands[1,5,6,12–21] in part because they may act as a 1- or

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Table I. Atomic Positions (×10⁴) for $[Ru(\eta^3\text{-PhCCCCHPh})(CO)_2(PPh_3)_2]PF_6$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ru(1)	1250.6 (5)	3405.8 (4)	5073.5 (4)	C(121)	1563 (5)	1920 (4)	6877 (3)
Ru(2)	2447.1 (4)	6588.3 (4)	704.9 (4)	C(132)	−864 (4)	3476 (4)	3576 (4)
P(11)	2701.2 (15)	4475.9 (14)	5854.4 (12)	C(133)	−1554 (4)	3730 (4)	3131 (4)
P(21)	3081.9 (14)	5516.6 (14)	1052.5 (11)	C(134)	−2466 (4)	3215 (4)	2861 (4)
P(22)	1838.6 (15)	7667.9 (14)	341.5 (12)	C(135)	−2688 (4)	2447 (4)	3036 (4)
P(12)	−194.5 (16)	2337.6 (14)	4275.1 (13)	C(136)	−1999 (4)	2193 (4)	3481 (4)
Cl(11)	1819 (2)	160 (2)	9491 (2)	C(131)	−1087 (4)	2708 (4)	3751 (4)
Cl(12)	274 (3)	648 (3)	9304 (2)	C(142)	−1110 (5)	800 (4)	4469 (3)
Cl(21)	5461 (4)	37 (3)	12242 (3)	C(143)	−1577 (5)	313 (4)	4809 (3)
Cl(22)	5549 (6)	925 (3)	13517 (3)	C(144)	−1676 (5)	686 (4)	5405 (3)
C(991)	1363 (9)	720 (9)	9932 (7)	C(145)	−1307 (5)	1546 (4)	5661 (3)
C(992)	4823 (12)	366 (10)	12618 (9)	C(146)	−840 (5)	2033 (4)	5321 (3)
P(13)	−409.4 (17)	3874.3 (17)	7270.1 (13)	C(141)	−742 (5)	1660 (4)	4725 (3)
F(131)	−77.1 (17)	3154.3 (17)	7554.9 (13)	C(152)	−264 (4)	1860 (4)	2906 (4)
F(132)	−741.6 (17)	4594.2 (17)	6985.5 (13)	C(153)	−94 (4)	1417 (4)	2388 (4)
F(133)	−1317.9 (17)	3209.7 (17)	6663.6 (13)	C(154)	269 (4)	792 (4)	2553 (4)
F(134)	499.2 (17)	4539.0 (17)	7876.7 (13)	C(155)	463 (4)	610 (4)	3237 (4)
F(135)	−890.2 (17)	3872.8 (17)	7810.3 (13)	C(156)	293 (4)	1054 (4)	3755 (4)
F(136)	71.5 (17)	3875.9 (17)	6730.2 (13)	C(151)	−71 (4)	1679 (4)	3590 (4)
P(23)	3849.0 (18)	2206.9 (17)	11858.5 (14)	C(162)	2308 (3)	4558 (3)	7081 (3)
F(231)	2892.0 (18)	2246.0 (17)	11791.7 (14)	C(163)	2522 (3)	4834 (3)	7817 (3)
F(232)	4806.1 (18)	2167.5 (17)	11925.0 (14)	C(164)	3419 (3)	5307 (3)	8298 (3)
F(233)	4349.5 (18)	2981.1 (17)	12530.0 (14)	C(165)	4103 (3)	5504 (3)	8044 (3)
F(234)	3348.6 (18)	1432.4 (17)	11187.0 (14)	C(166)	3889 (3)	5228 (3)	7308 (3)
F(235)	3823.2 (18)	1607.8 (17)	12392.6 (14)	C(161)	2992 (3)	4756 (3)	6827 (3)
F(236)	3874.8 (18)	2805.9 (17)	11324.4 (14)	C(172)	3991 (4)	3694 (4)	6265 (3)
O(11)	194 (4)	4391 (4)	5464 (3)	C(173)	4630 (4)	3374 (4)	6171 (3)
O(12)	1407 (5)	4110 (4)	3786 (4)	C(174)	4894 (4)	3516 (4)	5605 (3)
O(21)	637 (4)	5608 (4)	700 (3)	C(175)	4519 (4)	3977 (4)	5134 (3)
O(22)	2075 (5)	5871 (4)	−870 (3)	C(176)	3881 (4)	4297 (4)	5229 (3)
C(11)	610 (6)	4039 (5)	5335 (5)	C(171)	3617 (4)	4156 (4)	5794 (3)
C(12)	1330 (6)	3862 (5)	4258 (5)	C(182)	3778 (3)	6040 (4)	5865 (3)
C(13)	1999 (5)	2498 (5)	4932 (5)	C(245)	1372 (4)	8467 (3)	2079 (3)
C(14)	1807 (6)	2427 (5)	5465 (5)	C(246)	1432 (4)	7983 (3)	1516 (3)
C(15)	1434 (5)	2695 (5)	5903 (5)	C(241)	1818 (4)	8362 (3)	1077 (3)
C(16)	1298 (6)	2531 (5)	6481 (5)	C(252)	2117 (4)	8132 (4)	−850 (3)
C(21)	1310 (6)	5975 (5)	698 (4)	C(253)	2609 (4)	8593 (4)	−1189 (3)
C(22)	2182 (6)	6131 (6)	−298 (5)	C(254)	3441 (4)	9227 (4)	−768 (3)
C(23)	3983 (5)	7504 (5)	961 (5)	C(255)	3782 (4)	9401 (4)	−10 (3)
C(24)	3743 (5)	7552 (5)	1521 (4)	C(256)	3291 (4)	8940 (4)	328 (3)
C(25)	3146 (6)	7294 (5)	1828 (4)	C(251)	2458 (4)	8306 (4)	−92 (3)
C(26)	3089 (6)	7432 (5)	2456 (5)	C(262)	2616 (3)	5444 (3)	2244 (3)
C(112)	2306 (5)	2518 (4)	3838 (4)	C(263)	2632 (3)	5183 (3)	2875 (3)
C(113)	2687 (5)	2248 (4)	3392 (4)	C(264)	3176 (3)	4719 (3)	3169 (3)
C(114)	3167 (5)	1705 (4)	3585 (4)	C(265)	3705 (3)	4514 (3)	2832 (3)
C(115)	3266 (5)	1434 (4)	4224 (4)	C(266)	3690 (3)	4775 (3)	2201 (3)
C(116)	2885 (5)	1705 (4)	4670 (4)	C(261)	3145 (3)	5240 (3)	1907 (3)
C(111)	2405 (5)	2247 (4)	4477 (4)	C(272)	4965 (4)	6287 (3)	1805 (2)
C(122)	2092 (5)	1491 (4)	6727 (3)	C(273)	5854 (4)	6608 (3)	1856 (2)
C(123)	2298 (5)	896 (4)	7108 (3)	C(274)	6027 (4)	6474 (3)	1239 (2)
C(124)	1974 (5)	729 (4)	7639 (3)	C(275)	5311 (4)	6019 (3)	571 (2)
C(125)	1445 (5)	1158 (4)	7789 (3)	C(276)	4422 (4)	5698 (3)	520 (2)
C(126)	1239 (5)	1753 (4)	7408 (3)	C(271)	4249 (4)	5833 (3)	1137 (2)
C(235)	−732 (4)	7587 (3)	−945 (4)	C(282)	1606 (4)	4295 (3)	−103 (3)
C(236)	155 (4)	7837 (3)	−402 (4)	C(283)	1166 (4)	3526 (3)	−599 (3)
C(231)	659 (4)	7308 (3)	−336 (4)	C(284)	1633 (4)	2972 (3)	−597 (3)
C(242)	2144 (4)	9225 (3)	1203 (3)	C(285)	2540 (4)	3188 (3)	−99 (3)
C(243)	2084 (4)	9709 (3)	1766 (3)	C(286)	2980 (4)	3957 (3)	397 (3)
C(244)	1698 (4)	9330 (3)	2205 (3)	C(281)	2513 (4)	4511 (3)	395 (3)
C(183)	3927 (3)	6813 (4)	5691 (3)	C(211)	4497 (3)	7732 (4)	605 (3)
C(184)	3187 (3)	7024 (4)	5268 (3)	C(222)	4683 (6)	8411 (5)	3201 (4)
C(185)	2298 (3)	6463 (4)	5020 (3)	C(223)	5333 (6)	8978 (5)	3847 (4)
C(186)	2150 (3)	5690 (4)	5194 (3)	C(224)	5099 (6)	9143 (5)	4426 (4)
C(181)	2890 (3)	5479 (4)	5616 (3)	C(225)	4216 (6)	8741 (5)	4359 (4)
C(212)	4183 (3)	7497 (4)	−150 (3)	C(226)	3566 (6)	8174 (5)	3713 (4)
C(213)	4777 (3)	7761 (4)	−480 (3)	C(221)	3800 (6)	8009 (5)	3134 (4)
C(214)	5685 (3)	8261 (4)	−55 (3)	C(232)	276 (4)	6528 (3)	−812 (4)
C(215)	5999 (3)	8497 (4)	700 (3)	C(233)	−610 (4)	6277 (3)	−1355 (4)
C(216)	5405 (3)	8232 (4)	1030 (3)	C(234)	−1115 (4)	6807 (3)	−1421 (4)

3-electron donor (Chart I). We sought an alternative and more general route to these ligands to the established methods based on hydrometalation of butadiynes, coupling of bis(alkynyl)mercurials, and vinylidene/acetylide coupling reactions (Scheme II). Accordingly, protonation reactions of the electron-rich complex $[Ru(CO)_2(PPh_3)_2(Ph{-}C{\equiv}C{-}C{\equiv}C{-}Ph)]$ (1) were investigated.

Addition of excess hydrochloric acid leads to cleavage of the diyne from the metal center and the only organometallic product isolated (in high yield) was *cis*-$[RuCl_2$-

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Table II. Selected Bond Lengths (Å) and Angles (deg) for the Salt $[Ru(\eta^3\text{-}PhCCCCHPh)(CO)_2(PPh_3)_2]PF_6$ (Esd's Given in Parentheses)

molecule 1		molecule 2	
Ru(1)–P(11)	2.423 (2)	Ru(2)–P(21)	2.427 (3)
Ru(1)–P(12)	2.424 (2)	Ru(2)–P(22)	2.423 (3)
Ru(1)–C(11)	1.892 (12)	Ru(2)–C(21)	1.896 (10)
Ru(1)–C(12)	1.939 (11)	Ru(2)–C(22)	1.941 (11)
Ru(1)–C(13)	2.320 (10)	Ru(2)–C(23)	2.322 (8)
Ru(1)–C(14)	2.233 (10)	Ru(2)–C(24)	2.232 (6)
Ru(1)–C(15)	2.170 (9)	Ru(2)–C(25)	2.170 (8)
C(11)–O(11)	1.124 (14)	C(21)–O(21)	1.130 (12)
C(12)–O(12)	1.125 (14)	C(22)–O(22)	1.128 (13)
C(13)–C(14)	1.244 (16)	C(23)–C(24)	1.251 (15)
C(14)–C(15)	1.371 (16)	C(24)–C(25)	1.362 (14)
C(15)–C(16)	1.319 (14)	C(25)–C(26)	1.313 (14)
P(11)–Ru(1)–P(12)	179.1 (1)	P(21)–Ru(2)–P(22)	178.5 (1)
C(11)–Ru(1)–C(12)	97.7 (4)	C(21)–Ru(2)–C(22)	97.8 (4)
Ru(1)–C(15)–C(16)	147.5 (8)	Ru(2)–C(25)–C(26)	145.5 (6)
Ru(1)–C(15)–C(14)	74.4 (6)	Ru(2)–C(25)–C(24)	74.5 (5)
Ru(1)–C(13)–C(111)	141.0 (7)	Ru(2)–C(23)–C(211)	139.2 (5)
Ru(1)–C(13)–C(14)	70.3 (7)	Ru(2)–C(23)–C(24)	70.1 (5)
Ru(1)–C(14)–C(15)	69.4 (6)	Ru(2)–C(24)–C(25)	69.5 (4)
Ru(1)–C(14)–C(13)	78.0 (6)	Ru(2)–C(24)–C(23)	78.1 (4)
C(13)–C(14)–C(15)	147.4 (10)	C(23)–C(24)–C(25)	147.6 (7)

$(CO)_2(PPh_3)_2]$. In a similar reaction, the complex $[Ru(CO)_2(PPh_3)_2(OSNC_6H_4Me\text{-}4)]$ treated with hydrochloric acid led to cleavage of the iminooxosulfurane; however the use of acids of nonnucleophilic anions (HBF_4, $HSbF_6$ or $HClO_4$) allowed isolation of the intermediates in the protonolysis.[22] Thus treating $[Ru(CO)_2(PPh_3)_2(\eta^2\text{-}Ph\text{—}C{\equiv}C\text{—}C{\equiv}CPh)]$ with perchloric acid in a mixture of dichloromethane and ethanol leads to the salt $[Ru(\eta^3\text{-}PhC{\equiv}C\text{—}C{=}CHPh)(CO)_2(PPh_3)_2]ClO_4$ ($2\cdot ClO_4$). Similar salts ($2\cdot BF_4$ and $2\cdot PF_6$) are formed with tetrafluoroboric or hexafluorophosphoric acids.

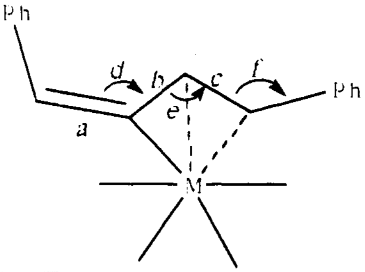
The initial site of protonation in this reaction is not clear because protonation at either the ruthenium center or directly at the alkyne carbon would lead to the same product. Protonation at the metal center could in principle lead to two possible stereochemistries, with either *cis*- or *trans*-dicarbonyl geometry. The latter would position the ruthenium hydride trans to the alkyne and therefore prevent hydroruthenation of the alkyne; however since the alkyne is a strong π-acid, protonation at the metal would be expected to occur cis to this ligand. Protonation of the complex $[Ru(CO)_2(CNC_6H_4Me\text{-}4)(PPh_3)_2]$ occurs trans to the poorest π-acid[23] to give *trans-trans*-$[RuH(CO)_2(CNC_6H_4Me\text{-}4)(PPh_3)_2]^+$. Protonation directly on the alkyne would produce a σ–π-vinyl ligand which could then rearrange to allow π-coordination of the α-phenylethynyl group (Scheme III).

An alternative synthesis of the complex $[Ru(\eta^3\text{-}PhC{\equiv}C\text{—}C{=}CHPh)(CO)_2(PPh_3)_2]^+$ was also developed beginning with the coordinatively unsaturated σ-vinyl complex $[Ru\{\eta^1\text{-}C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$.[5] A solution of this complex in dichloromethane reacts with carbon monoxide to provide $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)_2(PPh_3)_2]$, the chloride of which is labile and easily abstracted with silver tetrafluoroborate or hexafluorophosphate to provide $2\cdot BF_4$ or $2\cdot PF_6$. Because the complex $[Ru\{\eta^1\text{-}C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$ is prepared in high yield from $[RuClH(CO)(PPh_3)_3]$, this latter route to cationic complexes of the 1-en-3-yn-2-yl ligand is preferable since it avoids the oxygen-sensitive intermediate $[Ru(CO)_2(PPh_3)_3]$ (prepared in three steps from $[RuClH(CO)(PPh_3)_3]$[7]). All steps in the alternative synthesis may be carried out under aerobic conditions and proceed in high yield.

Spectroscopic data for the complex suggest that the enynyl ligand is *trihapto* coordinated: The FAB-mass spectrum shows a well-defined molecular ion with no indication of perchlorate or hexafluorophosphate binding. The infrared data associated with the perchlorate counteranion for $2\cdot ClO_4$ are consistent with this anion being uncoordinated. The band due to $\nu(C{\equiv}C_{free})$ apparent in the spectrum of 1 is absent in those of the salts of cation 2^+ although this band is sometimes weak and not reliably diagnostic.

From a reactivity point of view the trihapto formulation of the 1-en-3-yn-2-yl ligand is supported by the ability of the complex cation 2^+ to coordinate 2-electron ligands (vide infra); however we note that the complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$[5] and the crystallography characterized complex $[Ru\{C(C{\equiv}CCMe_3){=}CHCMe_3\}Cl(CO)(PPh_3)_2]$[21] both coordinate 2-electron ligands but show ground-state structures with coordinatively unsaturated metal centers and η^1-enynyl ligands. We could therefore not rule out a similarly unsaturated structure for 2^+ and so a crystal structure determination of $2\cdot PF_6$ was undertaken, the results of which are shown in Figure 1 and Tables I and II and are discussed later.

Table III. Structural Data for the Complexes $L_4M\{\eta^3\text{-}PhC{\equiv}C\text{—}C{=}CHPh\}$



L_nM[a]	a (Å)	b (Å)	c (Å)	d (deg)	e (deg)	f (deg)
$[Ru(CO)_2L'_2]^+$ (molecule 1)	1.319	1.371	1.244	138.1	147.4	148.7
$[Ru(CO)_2L'_2]^+$ (molecule 2)	1.313	1.362	1.251	140.1	147.6	150.6
$[Os(PMe_3)_4]^+$	1.32	1.39	1.29	132	150	149
$[Fe(dmpe)_2]^+$	1.338	1.396	not given	132.5	149.1	152.9
[RuCl(Cyttp)] (syn-*mer*)	1.335	1.416	1.220	129.2	154.3	156.7
[RuCl(Cyttp)] (anti-*mer*)	1.343	1.396	1.248	130.4	148.2	147.0
[Ru(C≡CPh)(Cyttp)] (*mer*)	1.339	1.379	1.249	133.1	148.7	144.6

[a] $L' = PPh_3$; dmpe = $Me_2PCH_2CH_2PMe_2$; Cyttp = $PhP\{CH_2CH_2CH_2P(C_6H_{11})_2\}_2$.

Table IV. Infrared and Microanalytical Data for the Complexes, $\{\text{Ru}\} = \text{Ru(CO)}_2(\text{PPh}_3)_2$

compd	infrared[a] (cm^{-1}) ν(CO)	infrared[a] (cm^{-1}) other	%[b] C	%[b] H	%[b] N
$[\{\text{Ru}\}(\text{PhC}{\equiv}\text{CC}{\equiv}\text{CPh})]^c$ **1**, yellow	1978, 1908 (1978, 1917)	2136 (2145) [ν(C≡C)], 1742 (1741) [ν(C≡C)]	68.4 (68.2)	4.3 (4.4)	
$[\{\text{Ru}\}\{\text{CC}{\equiv}\text{CPh}{=}\text{CHPh}\}]\text{PF}_6{}^d$ (**2**·PF$_6$), yellow	2052, 2001 (2052, 2004)		61.5 (61.5)	3.9 (3.9)	
$[\{\text{Ru}\}\{\text{CC}{\equiv}\text{CPh}{=}\text{CHPh}\}(\text{NCMe})]\text{PF}_6$ (**3a**·PF$_6$), yellow	2060, 2001 (2061, 2008)	2324, 2296 [ν(C≡N)], 2160 (2162) [ν(C≡C)]	62.6 (62.8)	4.2 (4.1)	1.0 (1.3)
$[\{\text{Ru}\}\{\text{CC}{\equiv}\text{CPh}{=}\text{CHPh}\}(\text{CN}^t\text{Bu})]\text{PF}_6$ (**3b**·PF$_6$), yellow	2065, 2022 (2068, 2025)	2204 (2200) [ν(CN)], 2169 (2160)	60.6 (60.2)	4.3 (4.3)	1.2 (1.2)
$[\{\text{Ru}\}\{\text{CC}{\equiv}\text{CPh}{=}\text{CHPh}\}(\text{CNC}_6\text{H}_3\text{Me}_2)]\text{PF}_6{}^d$ (**3c**·PF$_6$), purple	2073, 2026 (2068, 2028)	2176 (2176) [ν(CN)]	63.9 (63.4)	4.2 (4.3)	1.2 (1.2)
$[\{\text{Ru}\}\{\text{CC}{\equiv}\text{CPh}{=}\text{CHPh}\}\text{Cl}]$ (**4a**), yellow	2036, 1972 (2040, 1975)	2155 (2157) [ν(C≡C)]	69.9 (70.5)	4.4 (4.5)	
$[\{\text{Ru}\}\{\text{CC}{\equiv}\text{CPh}{=}\text{CHPh}\}\text{N}_3]^d$ (**4b**), yellow	2020, 1975 (2031, 1974)	2051 (2059) [ν(N$_3$)], 2153 (2158) [ν(C≡C)]	67.1 (67.5)	4.7 (3.4)	3.6 (4.3)

[a] Data were obtained from Nujol mulls between KBr disks in the range 4000–400 cm^{-1}. Data in parentheses are for dichloromethane solutions 1700–2300 cm^{-1}. [b] Calculated values given in parentheses. [c] Crystallizes as a dichloromethane monosolvate by ^{1}H NMR integration. [d] Crystallizes as a dichloromethane hemisolvate by ^{1}H NMR integration.

Table V. ^{31}P and ^{1}H NMR Data for the Complexes,[a] $\{\text{Ru}\} = \text{Ru(CO)}_2(\text{PPh}_3)_2$

compd	^{31}P (δ)	^{1}H (δ)
$[\{\text{Ru}\}(\text{PhC}{\equiv}\text{CC}{\equiv}\text{CPh})]$ (**1**)	43.8	
$[\{\text{Ru}\}\{\text{C(C}{\equiv}\text{CPh)}{=}\text{CHPh}\}]\text{PF}_6$ (**2**·PF$_6$)	32.8	6.91 [s, 1 H, =C*H*Ph]
$[\{\text{Ru}\}\{\text{C(C}{\equiv}\text{CPh)}{=}\text{CHPh}\}(\text{NCMe})]\text{PF}_6$ (**4a**·PF$_6$)	28.3, 29.2	6.6 s (v, br), 1 H, =C*H*Ph], 1.99 (s, 3 H, NCC*H*$_3$)
$[\{\text{Ru}\}\{\text{C(C}{\equiv}\text{CPh)}{=}\text{CHPh}\}(\text{CN}^t\text{Bu})]\text{PF}_6$ (**4b**·PF$_6$)	27.2	6.02 (s, 1 H, =C*H*Ph), 1.06 (s, 9 H, NC(C*H*$_3$)$_3$)
$[\{\text{Ru}\}\{\text{C(C}{\equiv}\text{CPh)}{=}\text{CHPh}\}(\text{CNC}_6\text{H}_3\text{Me}_2)]\text{PF}_6$ (**4c**·PF$_6$)	26.2	6.24 (s, 1 H, =C*H*Ph), 1.89 (s, 6 H, C$_6$H$_3$(C*H*$_3$)$_2$)
$[\{\text{Ru}\}\{\text{C(C}{\equiv}\text{CPh)}{=}\text{CHPh}\}\text{Cl}]$ (**3**)	24.9	6.45 (s, 1 H, =C*H*Ph)
$[\{\text{Ru}\}\{\text{C(C}{\equiv}\text{CPh)}{=}\text{CHPh}\}\text{N}_3]$ (**5**)	27.3	6.04 (s, 1 H, =C*H*Ph)

[a] From saturated solutions of the complex in CDCl$_3$ at ambient temperature. Chemical shifts are given relative to internal Me$_4$Si or external 85% H$_3$PO$_4$ (0.00 ppm).

The molecular structure of the cation **2**$^+$ shows that indeed the trihapto coordination mode is adopted, *at least in the solid state*; however the facile reactions of the salt (**2**·PF$_6$) with donor ligands suggests that this coordination is weak and reversible, i.e., *hemilabile*. Treating **2**·PF$_6$ with acetonitrile leads to the reversible formation of $[\text{Ru}\{\eta^1\text{-C(C}{\equiv}\text{CPh)}{=}\text{CHPh}\}(\text{CO})_2(\text{NCMe})(\text{PPh}_3)_2]\text{ClO}_4$ (**4a**·PF$_6$). When this adduct is recrystallized in the absence of excess acetonitrile, the nitrile is readily lost from the coordination sphere and the precursor complex **2**$^+$ is isolated. In complex **4a**$^+$ the acetonitrile ligand coordinates cis to the η^1-C(C≡CPh)=CHPh group, as suggested by the appearance of two ν(CO) associated bands in the infrared spectra of the salt. These bands are however not shifted significantly from those of **2**·PF$_6$, suggesting that the hemilabile alkyne functions primarily as a donor. The ^{31}P NMR spectrum of **4a**·PF$_6$ shows two singlet peaks of equal intensity suggesting two isomers exist in solution. Since there is no coupling observed between the phosphorus signals both isomers must have the phosphines in chemically equivalent environments. Solution (CH$_2$Cl$_2$) infrared data discount the possibility of a *trans*-dicarbonylruthenium stereochemistry. It would therefore appear that the isomerism is associated with the disposition of the nitrile ligand relative to the α-alkynyl substituent of the η^1-vinyl ligand. Rotation about the Ru—C bond of the σ-vinyl ligand would be prevented by a steric clash with the axial phosphine ligands once the nitrile ligand had coordinated to intermediate complex $[\text{Ru}\{\eta^1\text{-C(C}{\equiv}\text{CPh)}{=}\text{CHPh}\}(\text{CO})_2(\text{PPh}_3)_2]^+$ and approach of the nitrile must be equally favorable from either side of the σ-vinyl ligand.

Carbon monoxide fails to coordinate appreciably under mild conditions (1 atm, room temperature), with no spectroscopic data being obtained to support the formation of $[\text{Ru}\{\eta^1\text{-C(C}{\equiv}\text{CPh)}{=}\text{CHPh}\}(\text{CO})_3(\text{PPh}_3)_2]\text{ClO}_4$. It is noteworthy that the complex *mer*-$[\text{Ru}\{\text{C(=O)C}_2\text{H}_5\}(\text{CO})_3(\text{PPh}_3)_2]^+$ forms readily from $[\text{Ru}\{\text{C(=O)C}_2\text{H}_5\}\text{Cl(CO)}_2(\text{PPh}_3)_2]$ and silver perchlorate in the presence of carbon monoxide,[24] despite the ability of propionyl ligands to stabilize reduced coordination in this system by *dihapto* 3-electron donation. Presumably the trihapto 3-electron coordination of the enynyl ligand is favored over formation of a σ-vinyl tricarbonyl complex even though it might be expected that the propionyl ligand is more electron withdrawing than a σ-vinyl ligand. The reaction of the σ-vinyl complexes $[\text{Ru(vinyl)Cl(CO)(PPh}_3)_2]$ with carbon monoxide lead to the formation of either dicarbonyl complexes $[\text{Ru(vinyl)Cl(CO)}_2(\text{PPh}_3)_2]$ or enoyl complexes $[\text{Ru}\{\eta^2\text{-C(=O)vinyl}\}\text{Cl(CO)(PPh}_3)_2]$ via migratory insertion reactions,[25] a reactivity pattern previously established for the σ-tolyl derivatives $[\text{Ru(C}_6\text{H}_4\text{Me-4)X(CO)(PPh}_3)_2]$ (X = Cl, Br, I).[26] In general we have found the enynyl ligand in these systems to be reluctant to enter into migratory insertion reactions, presumably due to steric pressures.[5]

Stable adducts of (**2**·PF$_6$) may be obtained by treating the salt with isonitriles: *tert*-butyl isocyanide and 2,6-dimethylphenyl isocyanide coordinate to provide complexes with monohapto 1-en-3-yn-2-yl ligands, viz. $[\text{Ru}\{\eta^1\text{-C(C}{\equiv}\text{CPh)}{=}\text{CHPh}\}(\text{CO})(\text{CNR})(\text{PPh}_3)_2]\text{ClO}_4$ (R = ^{t}Bu (**4b**·PF$_6$), C$_6$H$_3$Me$_2$-2,6 (**4c**·PF$_6$)). Once again two ν(CO) associated absorbances are observed in the infrared spectra of salts of **4b**$^+$ and **4c**$^+$, suggesting that coordination of the incoming ligand occurs cis to the σ-vinyl ligand consistent with the vacant site being produced by dissociation of the hemilabile alkyne group. These absorbances are, however,

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Scheme I. Synthesis and Protonation of the Complex $[Ru(CO)_2(PhCCCCPh)(PPh_3)_2]$: (i) PhCCCCPh; (ii) $HClO_4$; (iii) 1.0 HCl; (iv) CO; (v) excess HCl; (vi) LiX (X = N_3, Cl); (vii) CNR (R = $C_6H_3Me_2$-2,6; CMe_3)

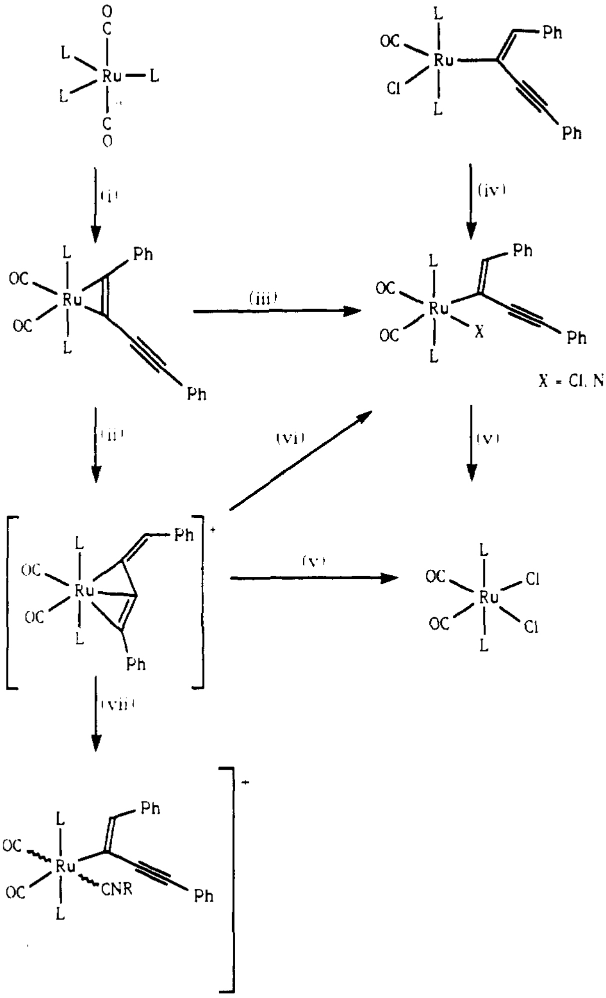
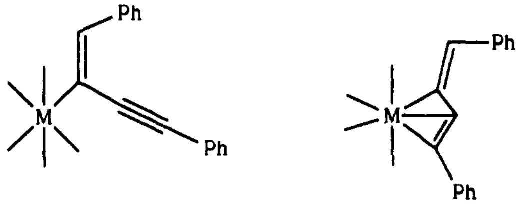


Chart I. Bonding Modes for the –C(C≡CPh)=CHPh Ligand



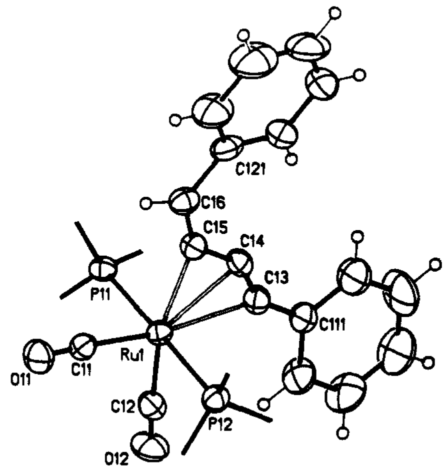


Figure 1. Molecular structure of $[Ru(\eta^3\text{-}PhCCCCHPh)(CO)_2(PPh_3)_2]^+$ (2^+) (molecule 1). Phosphine phenyl groups are omitted for clarity.

shifted to higher energy from those of 2^+ as expected for the π-acid role of the isonitrile ligands and in support of the suggestion (vide supra) that the hemilabile alkyne coordination involves a predominantly dative interaction. The appearance of singlet resonances in the ^{31}P NMR spectra of $3c^+$ and $3d^+$ suggest that either the vinyl ligand is static and lies in the plane of the carbonyl and isonitrile ligands or, less likely, rotates rapidly about the Ru–C bond. We have not observed any indication that migratory insertion processes involving either carbonyl or isonitrile ligands occur although such processes have been noted for simple σ-vinyl ligands in related systems.[25]

As noted above, chloride readily coordinates to the ruthenium center of 2·PF_6 restoring neutrality. This reaction is not limited to halides but other anions, e.g., azide, readily adds. Thus ethanolic suspensions of 2·PF_6 and sodium azide provide the azido complex $[Ru\{C(\equiv CPh)=CHPh\}N_3(CO)_2(PPh_3)_2]$ (**5**). The appearance of two ν(CO) associated infrared bands indicates that coordination has occurred cis to the σ-vinyl ligand, whilst the peak observed at 2051 cm^{-1} shows that the azido groups remains intact during coordination (Scheme IV).

We find the failure to observe any attack by nucleophiles at the somewhat unusually hybridized central carbon atom of the η^3-enynyl ligand surprising, and this is even more so in view of the very recent report by Casey and Yi of a related rhenium(III) complex $[Re(\eta^3\text{-}CH_2C{\equiv}CMe)(CO)_2(\eta\text{-}C_5Me_5)]^+$ which reacts with soft nucleophiles [PMe_3, LiC≡C^{t}Bu, $NaCH(CO_2Et)_2$] exclusively at the central carbon of the trihapto propargyl ligand.[27] The origin of this divergence in the reactivity of the two complexes $[Re(\eta^3\text{-}CH_2C{\equiv}CMe)(CO)_2(\eta\text{-}C_5Me_5)]^+$ and 2^+ may be due to the more electrophilic nature of the formally d^4 rhenium center causing more significant depopulation of the alkyne π^b orbital, relative to the d^6 ruthenium center. Alternatively, Casey has suggested, on the basis of NMR data for the methylene component of the propargyl ligand, that an η^3-allenyl resonance contributor (cf. B, Scheme V) might better describe the bonding in the rhenium complex. The structural data for 2·PF_6 better support a η^3-enynyl description (A, Scheme V) for the ruthenium complex (vide infra).

Description of the Structure of $[Ru(\eta^3\text{-}PhCCCCHPh)(CO)_2(PPh_3)_2]PF_6$ and Related Compounds. The crystal structure of 2·PF_6 shows two independent molecules within the asymmetric unit; however since the structural parameters for the two molecules are very similar we will only discuss that based on "Ru(1)". The ruthenium center approaches trigonal bipyramidal geometry if the η^3-vinyl ligand is considered as one substituent, with an intercarbonyl angle of 97.7°, between that expected for octahedral and trigonal bipyramidal geometries. The two ruthenium–carbon bond lengths for the two carbonyl ligands are significantly different (5σ), indicating different trans influences for the "vinyl" and "alkyne" ligands. Coordination of donor ligands trans to a carbonyl typically strengthens the metal–carbonyl interaction and this is consistent with spectroscopic data which were interpreted above as indicating a primarily donor role for the alkynyl group. The difference in ruthenium–carbonyl separations

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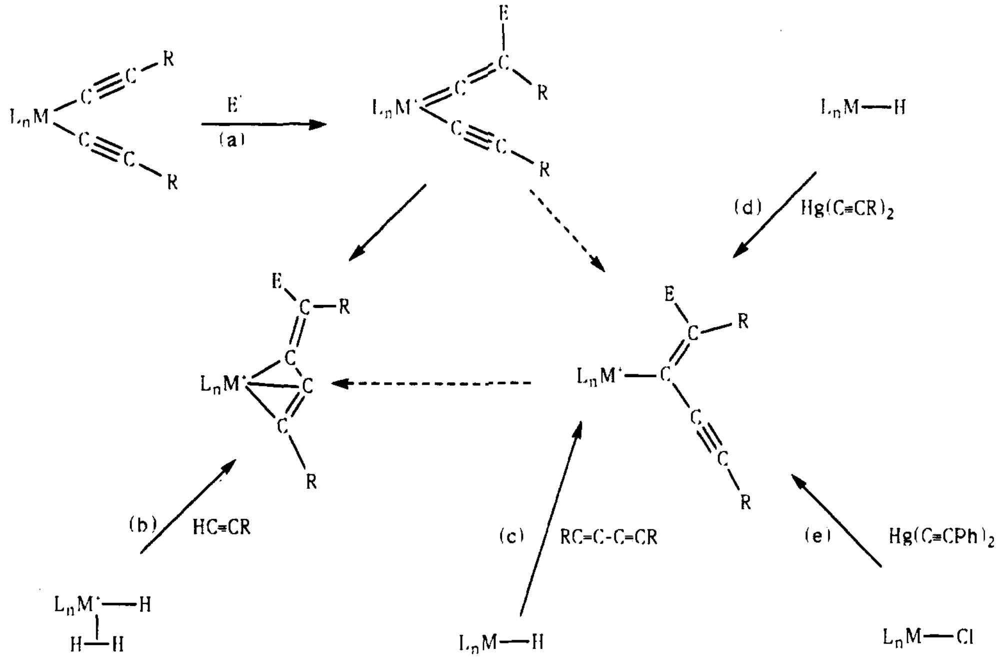
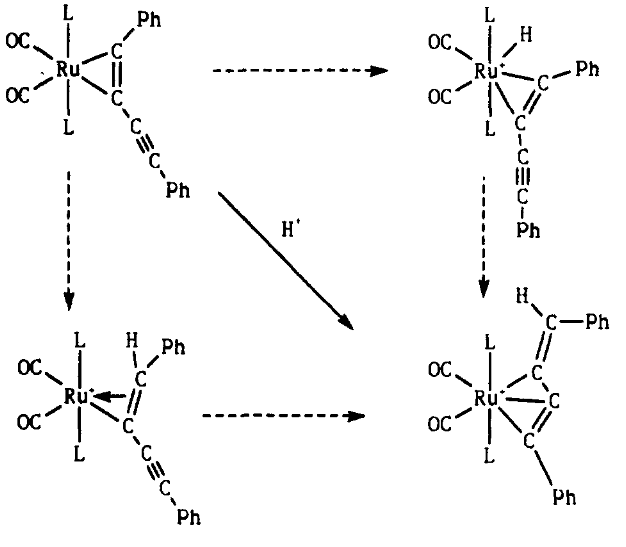
Scheme II. Synthetic Pathways to α-Alkynyl Vinyl Ligands[a]

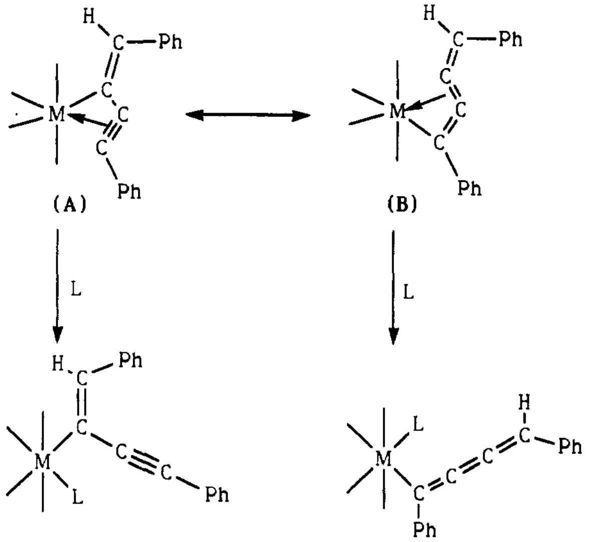


[a] (a) L$_n$M = Fe(dmpe)$_2$, E = H, R = Ph;[12] L$_n$M = Os(PMe$_3$)$_4$, E = H (Ag$^+$/H$^•$), R = Ph;[13] L$_n$M = W(CO)$_2$(η-C$_5$Me$_5$)$^-$, E = CH$_3$, R = CMe$_3$.[20] (b) L$_n$M = Fe(dmpe)$_2$, E = H, R = Ph;[18] L$_n$M = Ru{P(CH$_2$CH$_2$PPh$_2$)$_3$}, E = H, R = SiMe$_3$.[29] (c) L$_n$M = RuCl(CO)(PPh$_3$)$_2$, E = H, R = CMe$_3$,[21] R = Ph, SiMe$_3$, H, CMe$_2$OH, ^{n}Bu;[5,30] L$_n$M = Ru(O$_2$CCF$_3$)(CO)(PPh$_3$)$_2$, E = H, R = Ph;[9] L$_n$M = RuH$_3$(Cyttp), RuCl(Cyttp), E = H, R = Ph;[12,14,17] L$_n$M = RuCl(CO)(BSD)(PPh$_3$)$_2$, E = H, R = Ph, SiMe$_3$.[5,6,30] (d) L$_n$M = RuCl(CO)(PPh$_3$)$_2$; E = H, R = Ph, C$_6$H$_4$Me-4, ^{n}Bu, CMe$_2$OH. (e) L$_n$M = RuCl(CO)$_2$(PMe$_2$Ph)$_2$, E = HgCl, R = Ph.[32] Abbreviations: dmpe = 1,2-bis(dimethylphosphino)ethane; BSD = 2,1,3-benzoselenadiazole; Cyttp = PhP(CH$_2$CH$_2$PCy$_2$)$_2$; Cy = cyclohexyl.

Scheme III. Protonation of [Ru(η^2-PhC≡CC≡CPh)(CO)$_2$(PPh$_3$)$_2$] (L = PPh$_3$)



Scheme IV. Canonical Forms for the η^3-Bonding Mode of the PhC≡C—C═CHPh Ligand—Chemical Implications



may also be due to the recognized trans influence of σ-vinyl ligands. For example in the structurally chararcterized complex [Ru{C(C≡CPh)═CHPh}(CO)(PPh$_3$){HB(pz)$_3$}] (pz = pyrazol-1-yl)[15] the longest ruthenium–pyrazole separation is observed for the pyrazole coordinated trans to the η^1-enynyl ligand.

The most notable structural features of **2**·PF$_6$ are concerned with the "RuC$_3$" unit of the η^3-vinyl group, and structural parameters associated with this group are collected in Table III. Unfortunately, structural data for simple d^6 RuL$_5$ alkyne complexes is somewhat scarce; however there is now a substantial body of data available for complexes of the "C(C≡CPh)═CHPh" ligand and the majority of these are fortunately based on low-valent ruthenium systems. Thus the trihapto complexes [Ru{η^3-C(C≡CPh)═CHPh}(C≡CPh)(Cyttp)] (syn-*mer* and anti-*mer* forms), [Ru{η^3-C(C≡CPh)═CHPh}Cl(Cyttp)][12,14] [Cyttp = PhP(CH$_2$CH$_2$PCy$_2$)$_2$, Cy = cyclohexyl], and [Ru{η^3-C(C≡CPh)═CHPh}(CO)$_2$(PPh$_3$)$_2$]$^+$ (two crystallography independent molecules) provide in total five ruthenium-based examples for comparison. Table III also sumarizes pertinent data for the two other known examples [Os{η^3-C(C≡CPh)═CHPh}(PMe$_3$)$_4$]$^+$,[13] and [Fe{η^3-C(C≡CPh)═CHPh}(dmpe)$_2$]$^+$ [dmpe = 1,2-bis(dimethylphosphino)ethane];[16,18] however the complex [W{η^3-C(C≡CCMe$_3$)═CMeCMe$_3$}(CO)$_2$(η-C$_5$Me$_5$)][20] is omitted because direct comparison is less reliable due to the difference in central metal, the different substitution on the enynyl ligand, and the observed aplanarity of the "MC_3" unit.

Assuming that the bend-back angle of the phenyl substituent is the most sensitive parameter for assessing alkyne bonding and relating it to the alkyne carbon hybridization, we have chosen, in particular, this parameter to discuss the bonding within the "RuC_3" group. The bend-back angle (*f*, Table III) for simple diphenylacetylene complexes typically falls in the range 135–140°, and accordingly, those observed for the enynyl complexes are all larger than this, ranging from 144.6 to 156.7° for the ruthenium complexes, suggesting marginally more sp character in the hybridization of these alkynyl groups than in simple η^2-2-electron coordination. This is consistent with the idea that these alkynyl groups are weakly bound. Furthermore the alkynyl C≡C bond length (*c*, Table III) lies between 1.22 and 1.25 Å for the η^3-enynyl complexes and 1.21 and 1.22 Å for related monohapto enynyl ruthenium complexes.[15,19,21] Whilst there is clearly a lengthening of this bond upon coordination, it is not as marked as for conventional alkyne coordination where C≡C bonds are typically in the range 1.27–1.36 Å, the longer bond lengths being observed for 4-electron coordination.[28] The angle between vinyl and alkynyl substituents (*d*, Table III) is larger than the expected value of 120° for trigonal carbon found in monohapto complexes; however, this opening up to 130–140° is a geometric requirement.

Two valence bond descriptions have been suggested for the bonding of trihapto enynyl ligands (Scheme V). We prefer the canonical form A since this form is reflected in the chemistry of 2^+; i.e., 2-electron ligands readily open the metallacycle with displacement of an alkynyl group rather than a 1,2,3-trienyl unit which would be expected for form B. Furthermore, Table III shows that for all the complexes, the three C–C bonds fall in distinct nonoverlapping ranges consistent with fairly localized single (*b*), double (*a*), and triple (*c*) bonds.

Concluding Remarks

Whilst both η^1- and η^3-coordinated enynyl ligands are well-established and structurally characterized, the origin of these ligands has provided the central theme of previous studies and there has been only one attempt[29] to relate these two bonding modes since our original report.[5] Clearly, the results outlined herein show that the two modes may under favorable circumstances be interconverted, depending on the electronic requirements of the central metal and the properties of potential ligands available for the replacement of what appears to be a weak coordination of the alkyne group. Questions still remain, the most conspicuous being the failure of the alkyne group to coordinate in the 16-electron complexes [Ru{C(C≡CR)=CHR}Cl(CO)(PPh_3)$_2$] for no apparent reason. It is perhaps noteworthy that simple vinyl ligands bound to the "RuCl(CO)(PPh_3)$_2$" fragment also show no tendency to enter into σ–π or *agostic* β-H coordination although these methods of alleviating coordinative unsaturation are adopted in other metal ligand systems.

We are currently investigating the generalization of this class of ligands to other metal centers, electronic configurations, and vinyl substituents to better understand this unusual type of bonding in addition to developing alternative routes.

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Supplementary Material Available: Tables of atom coordinates, anisotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and calculated H-atom coordinates (13 pages). Ordering information is given on any current masthead page.

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