Organometallics **2005,** *24,* 5795−5798

A Bimetallic Complex Spanned by the C_4H Ligand: Synthesis of $[Cl(CO)_2L_2RuC{\equiv}CCH{=}C{=}RuL_2(\eta\text{-}C_5H_5)]PF_6$ $(L = PPh_3)$

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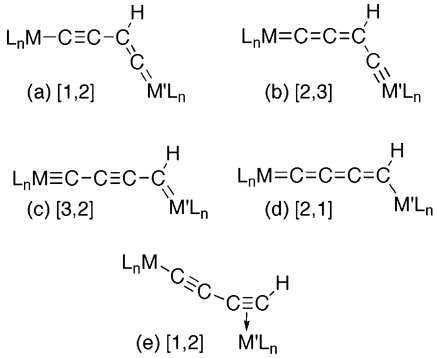
Received September 16, 2005

Summary: The synthesis of the first example of a bimetallic complex spanned by the C_4H alkynylvinylidene ligand, $[Cl(CO)_2L_2RuC{\equiv}CCH{=}C{=}RuL_2(\eta\text{-}C_5H_5)]PF_6$ ($L = PPh_3$), is reported: the reaction of $[Ru(CO)_2L_3]$ with butadiyne provides $[RuH(C{\equiv}CC{\equiv}CH)(CO)_2L_2]$, which is converted to the chloro derivative $[RuCl(C{\equiv}CC{\equiv}CH)(CO)_2L_2]$ by N-chlorosuccinimide. Subsequent treatment with $[Ru(thf)L_2(\eta\text{-}C_5H_5)]PF_6$ provides $[Cl(CO)_2L_2RuC{\equiv}CCH{=}C{=}RuL_2(\eta\text{-}C_5H_5)]PF_6$, deprotonation of which affords $[Cl(CO)_2L_2RuC{\equiv}CC{\equiv}CRuL_2(\eta\text{-}C_5H_5)]$.

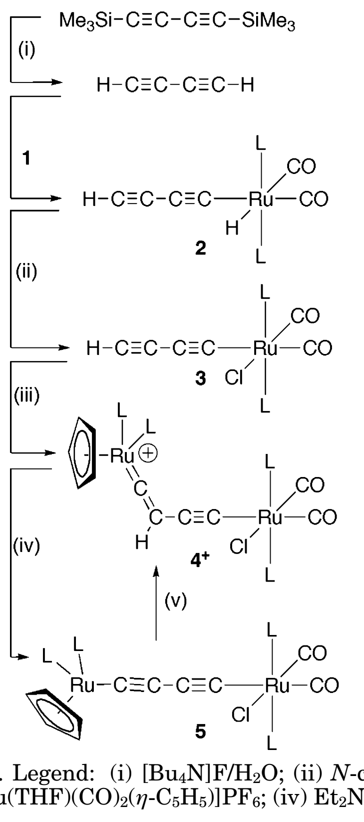
While there has been enormous and rapid progress in recent times in the synthesis of dimetalated butadiynes, $L_nM{-}(C{\equiv}C)_2{-}ML_n$,[1] far less is known about how partially reduced carbon chains, e.g., C_4H or C_4H_2, might bridge two metal centers. For C_4H Chart 1 presents how one might envisage possible coordination modes on the basis of the number of valence electrons [x,y] provided to each metal terminus and the position of the single-proton substituent. One complex in which two metals are spanned by a C_4H ligand has been reported from the reaction of $[W(C{\equiv}CC{\equiv}CH)(CO)_3(\eta\text{-}C_5H_5)]$ with $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$, in which the unstable product is suggested to adopt coordination mode e.[2] Protonation of the complexes $[Fe_2(\mu\text{-}C_4)(CO)_2(R_2PCH_2CH_2PR_2)(\eta\text{-}C_5Me_5)_2]$ ($R = Ph$, ^iPr) has been suggested to provide examples of the butatrienylidene form d,[3] although spectroscopic data and the facile deprotonation are also consistent with form e. Of the various possibilities shown in Chart 1, it is the alkynyl−vinylidene form (a) with which this paper is concerned. Such a coordination mode is likely as an intermediate in the double-deprotonation reactions that have been reported for a range of bis(vinylidenes);[4] however, isolated examples have yet to be described. We report herein the multistep synthesis of one such complex.

Chart 1. Plausible Binuclear Bridging Modes for the C_4H Ligand and Associated Valence Electron Contributions [x,y]



The complex $[Ru(CO)_2(PPh_3)_3]$ (**1**)[5] is known to π-coordinate internal alkynes[6] and diynes,[7] to cyclocodimerize α,ω-diynes with CO,[8] and to cleave one *single* C−C bond of dimetallaoctatetraynes.[9] However, with termi-

Scheme 1[a]



[a] L = PPh$_3$. Legend: (i) $[Bu_4N]F/H_2O$; (ii) *N*-chlorosuccinimide; (iii) $[Ru(THF)(CO)_2(\eta\text{-}C_5H_5)]PF_6$; (iv) Et_2NH; (v) HPF_6.

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10.1021/om050800o CCC: \$30.25

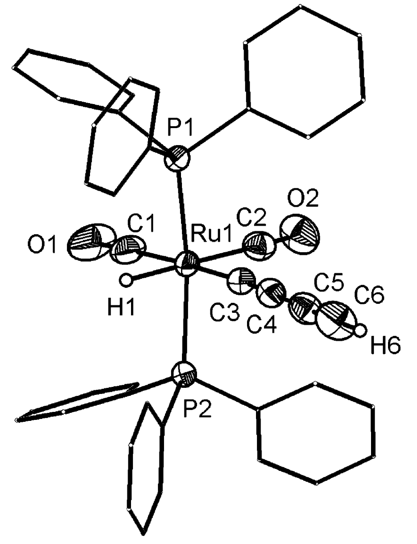

Figure 1. Molecular geometry of **2** in a crystal of **2**·C_6H_6 (phenyl groups simplified, 50% displacement ellipsoids). Selected bond distances (Å) and angles (deg): Ru1−C3 = 2.063(3), Ru1−P1 = 2.3557(9), Ru1−P2 = 2.3560(10), C3−C4 = 1.210(4), C5−C6 = 1.176(4), C5−C4 = 1.386(4), Ru1−H1 = 1.57(4), C6−H6 = 0.95(2); P1−Ru1−P2 = 168.00(3), C4−C3−Ru1 = 177.2(3), C6−C5−C4 = 178.7(3), C3−C4−C5 = 178.1(4).

nal alkynes C−H activation occurs with oxidative addition to provide hydrido−alkynyl derivatives of ruthenium(II).[5] We have therefore investigated the reaction of **1** with butadiyne (generated in situ from $Me_3SiC_4SiMe_3$ and moist $[Bu_4N]F$, "TBAF"), which proceeds to provide the complex $[RuH(C{\equiv}CC{\equiv}CH)(CO)_2(PPh_3)_2]$ (**2**) in 85% yield. Notably, there was no indication of the formation of the bimetallic derivative $(\mu\text{-}C_4)[RuH(CO)_2(PPh_3)_2]_2$ and isolated **2** did not react with a further equivalent of **1**. The characterization of **2**[10] included a crystallographic analysis, the results of which are summarized in Figure 1. The geometry at the octahedral ruthenium center is unremarkable, other than to confirm the stereochemistry inferred from spectroscopic data. Of the two C≡C triple bonds, that adjacent to ruthenium (C1−C2 = 1.210(4) Å) is somewhat longer (ca. 9σ) than the terminal one (C3−C4 = 1.176(4) Å), consistent with a retrodative role for the ruthenium center, despite the disposition of a carbonyl ligand trans to C1.

The complex **2** was found to decompose[11] during the time required for the acquisition of $^{13}C\{^1H\}$ NMR data; however, the more stable derivative $[RuCl(C{\equiv}CC{\equiv}CH)(CO)_2(PPh_3)_2]$ (**3**)[12] could be obtained via the reaction of **2** with *N*-chlorosuccinimide (NCS). Spectrocopic data for **3** are conclusive but generally unremarkable. Treating **3** with a filtered solution of $[Ru(THF)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (generated in situ from $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ and $AgPF_6$ in THF) provides the salt $[Cl(CO)_2L_2RuC{\equiv}CCH{=}C{=}RuL_2(\eta\text{-}C_5H_5)]PF_6$ (**4**-PF_6),[13] in which two ruthenium centers are linked in an unprecedented manner by the C_4H ligand bound to one ruthenium as a σ-alkynyl species and the other as a vinylidene (Scheme 1). The $^{13}C\{^1H\}$ NMR spectrum proved most diagnostic, revealing two alkynyl resonances (δ_C: 95.3; 127.7, t, $^2J_{PC} \approx 5.1$ Hz) in addition to those for the two carbons of the vinylidene linkage (δ_C: 120.3; 335.1, t, $^3J_{PC} = 10.9$ Hz). The vinylidene proton resonance was not directly observed in the ^1H NMR spectrum due to coincidence with the plethora of phenyl resonances; however, it could be identified (δ_H 7.26) by HMQC NMR measurements, which revealed a correlation with the resonance at δ_C 120.3.

In principle, the proton (the acidity of which is demonstrated below) could reside on either of the two carbons β to a ruthenium center (Chart 2). Vinylidene/1-alkyne tautomerism is particularly facile at divalent ruthenium centers, and it may therefore be assumed

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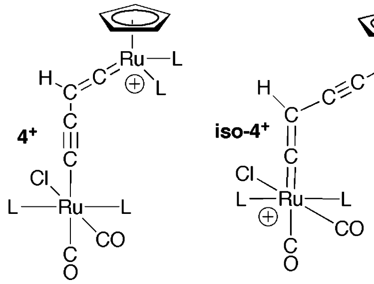
(10) **2**: to $Me_3SiC_4SiMe_3$ (2.47 g, 12.7 mmol) in ethanol (20 mL) was added $[Bu_4N]F$ (50.4 mL, 50.4 mmol, 1.00 mol L^{-1} in THF, Aldrich) and the mixture stirred for 15 min before anaerobic cannula transfer to a suspension of **1** (6.00 g, 6.35 mmol)[5b] in THF (100 mL). The mixture was stirred for 15 min and then concentrated to ca. 20 mL. The resulting white solid was isolated by filtration and recrystallized from CH_2Cl_2/EtOH to yield pale brown crystals. Yield: 3.96 g (85%). IR (CH_2Cl_2): 2143 ($\nu_{C{\equiv}C}$), 2040, 1987 (ν_{CO}), 1999 (ν_{RuH}) cm^{-1}. IR (Nujol): 2141 ($\nu_{C{\equiv}C}$), 2040, 1989 (ν_{CO}), 2004 (ν_{RuH}) cm^{-1}. NMR (C_6D_6, 25 °C): ^1H, δ_H − 5.30 (t, 1H, RuH, $^2J_{HP} = 20.0$), 1.21 (t, 1H, −C≡CH, $^6J_{HP} = 1.2$ Hz), 6.97, 7.92 (m × 2, 30H, C_6H_5); $^{31}P\{^1H\}$ δ_P 44.1. ESI-MS: *m/z* 772.8 $[M + H + NCMe]^+$. Anal. Found: C, 68.87; H, 4.79; N, 0.00. Calcd for $C_{42}H_{32}O_2P_2Ru$: C, 68.84; H, 4.40; N, 0.00. Crystal data for **2**·C_6H_6: $C_{48}H_{38}O_2P_2Ru$, $M_w = 809.79$, $P\bar{1}$ (No. 2), triclinic, $a = 10.010(2)$ Å, $b = 13.520(3)$ Å, $c = 15.669(3)$ Å, $\alpha = 100.96(3)°$, $\beta = 93.85(3)°$, $\gamma = 106.40(3)°$, $V = 1980.7(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.358$ Mg m^{-3}, $T = 200(2)$ K, colorless prism, F^2 refinement, R1 = 0.045, wR2 = 0.122, for 9060 independent observed absorption corrected reflections ($I > 2\sigma(I)$, $2\theta_{max} = 49.68°$), 478 parameters, CCDC 247962.

(11) If left to stand in solution under air, the complex **2** provides $[Ru(\eta^2\text{-}O_2)(CO)_2(PPh_3)_2]$, while under anaerobic conditions in the presence of PhC≡CPh the complex $[Ru(\eta^2\text{-}PhC{\equiv}CPh)(CO)_2(PPh_3)_2]$ slowly forms. Since these complexes are also the products of the reactions of **1** with air[5] and PhC≡CPh,[6] respectively, we conclude that **2** decomposes via reversible reductive elimination of butadiyne.

(12) **3**: *N*-chlorosuccinimide (0.04 g, 0.3 mmol) and **2** (0.18 g, 0.25 mmol) were dissolved in THF (30 mL) and the mixture stirred for 5 min. Ethanol was added, and the solvents were reduced to provide a pale yellow solid, which was isolated by filtration and recrystallized from CH_2Cl_2/EtOH to provide straw-colored crystals. Yield: 0.16 g (85%). IR (CH_2Cl_2): 2150 ($\nu_{C{\equiv}C}$), 2058, 1999 (ν_{CO}) cm^{-1}. IR (Nujol): 2147 ($\nu_{C{\equiv}C}$), 2057, 1997 (ν_{CO}) cm^{-1}. NMR (C_6D_6, 25 °C): ^1H, δ_H 1.43 (t, 1 H, C≡CH, $^6J_{HP} = 1.2$ Hz), 6.97, 8.19 (m × 2, 30 H, C_6H_5); $^{13}C\{^1H\}$, δ_C 58.3 (C≡*C*H), 71.9 (*C*≡CH), 97.3 (RuC≡*C*), 104.0 (t, $^2J_{CP} = 19.7$, Ru*C*≡C), 128.5 (vt, $J_{CP} = 4.98$, $C^{3,5}$ (C_6H_5)), 130.7 (C^4 (C_6H_5)), 132.9 (vt, $J_{CP} = 24.21$, C^1 (C_6H_5)), 134.4 (vt, $J_{CP} = 5.32$, $C^{2,6}$ (C_6H_5)), 191.7 (t, $^2J_{CP} = 8.98$, CO), 193.8 (t, $^2J_{CP} = 10.6$ Hz, CO); $^{31}P\{^1H\}$, δ_P 22.1. ESI-MS: *m/z* 806.8 $[M + NCMe]^+$. Anal. Found: C, 62.65; H, 4.04; N, 0.00. Calcd for $C_{42}H_{31}ClO_2P_2Ru{\cdot}0.66CH_2Cl_2$: C, 62.32; H, 3.97; N, 0.00 (CH_2Cl_2 estimated by ^1H NMR integration).

(13) **4**-PF_6: $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (0.10 g, 0.14 mmol) and $AgPF_6$ (0.035 g, 0.14 mmol) were stirred in THF (25 mL) for 10 min, the mixture was then transferred, via filter cannula, to a flask containing **3** (0.11 g, 0.14 mmol), and the resulting mixture was stirred for 10 min. The solvent volume was then reduced in vacuo and ethanol added to precipitate the orange-brown product, which was recrystallized from THF/ethanol as a THF monosolvate (^1H NMR). Yield: 0.17 g (75%). IR (CH_2Cl_2): 2052, 1994 (ν_{CO}), 1969 ($\nu_{C{=}C{=}Ru}$) cm^{-1}. IR (Nujol): 2046, 1986 (ν_{CO}), 1967 ($\nu_{C{=}C{=}Ru}$) cm^{-1}. NMR ($CHCl_3$, 25 °C): ^1H, δ_H 4.66 (s, 5H, C_5H_5), 7.11, 7.73, 7.78 (m × 3, 61 H, C_6H_5, and CH=C=Ru correlated to δ_C 120.3); $^{13}C\{^1H\}$, δ_C 91.4 (C_5H_5), 95.3 (RuC≡*C*), 120.3 (Ru=C=*C*H), 127.7 (t, $^2J_{PC} = 5.1$, Ru*C*≡C), 128.5 (vt, $J_{CP} = 4.00$, Ru_{CO} $C^{3,5}$ (C_6H_5)), 128.8 (vt, $J_{CP} = 5.13$, Ru_{Cp} $C^{3,5}$ (C_6H_5)), 130.5 (Ru_{CO} C^4 (C_6H_5)), 131.3 (Ru_{Cp} C^4 (C_6H_5)), Ru_{Cp} C^1 (C_6H_5) resonances obscured, 133.3 (vt, $J_{CP} = 5.21$, Ru_{Cp} $C^{2,6}$ (C_6H_5)), 133.3 (vt, $J_{CP} = 5.13$, Ru_{CO} $C^{2,6}$ (C_6H_5)), 191.9 (CO), 195.1 (CO), 335.1 (t, $^2J_{CP} = 10.9$ Hz, Ru=*C*=CH); $^{31}P\{^1H\}$, δ_P 23.4, 47.1. ESI-MS: *m/z* 1422.8 $[M - PF_6 - Cl]^+$. Anal. Found: C, 62.78; H, 4.43; N, 0.00. Calcd for $C_{83}H_{66}ClF_6O_2P_5Ru_2{\cdot}C_4H_8O$: C, 62.36; H, 4.45; N, 0.00.

Chart 2. Alternative Alkynyl−Vinylidene Tautomers: 4^+ and iso-4^+



that the adopted isomer in which Ru−C multiple bonding occurs specifically to the $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ end (**4^+** vs **iso-4^+**), represents the thermodynamic preference. This has been further confirmed by the observation that protonation of the butadiynediyl complex $[Cl(CO)_2(Ph_3P)_2RuC{\equiv}CC{\equiv}CRu(PPh_3)_2(\eta\text{-}C_5H_5)]$ (**5**; vide infra) with HPF_6 exclusively (re)generates **4**-PF_6, with no evidence for the transient intermediacy of **iso-4^+** being detectable within the time required to measure the ^{31}P NMR spectrum. Notably, the spectroscopic data associated with the $RuCl(CO)_2(PPh_3)_2$ terminus are essentially invariant in the sequence **3** → **4^+**, (δ_P: 22.1→23.4); indeed, the mean ν_{CO} value actually *decreases* marginally (mean ν_{CO}: 2027 → 2023 cm^{-1}), inconsistent with the formation of a cationic $[(Ph_3P)_2Cl(CO)_2Ru{=}CR_2]^+$ terminus.[14] Thus, structural changes may be assumed to be remote from the CO-ligated end of the metallacumulene. We have previously shown that the addition of CO trans to the vinylidene ligand in $[RuCl_2\{{=}C{=}C(Se^iPr)Ph\}(PPh_3)_2]$ results in rapid formation of $[RuCl_2(CO)_2(PPh_3)_2]$ (ttt isomer) and free $PhC{\equiv}CSe^iPr$.[15] In a similar manner, it has been noted that the reactions of electrophiles with the complex $[RuCl(C{\equiv}CPh)(CO)_2(PPh_3)_2]$ (an analogue of **3**) do not result in the formation of vinylidene derivatives, while HCl results in liberation of the alkyne and formation of $[RuCl_2(CO)_2(PPh_3)_2]$ (cct isomer).[16] Thus, any putative intermediate in which the superlatively π-acidic vinylidene ligand is coordinated trans to a carbonyl ligand at an octahedral ruthenium(II) center would appear to be destabilized due to competitive π-acceptance. Rearrangement of the vinylidene to an alkyne tautomer would alleviate this. However, this in turn introduces a further labilization resulting from the repulsive interaction of the filled alkyne bonding orbital (orthogonal to the RuC_2R_2 coordination plane) with the occupied $(t_{2g})^6$ set of metal orbitals. Thus, the stability of **4^+** and isomeric preference (cf. **iso-4^+**) may be traced to the disparate electronic natures of the two chemically distinct ruthenium termini.

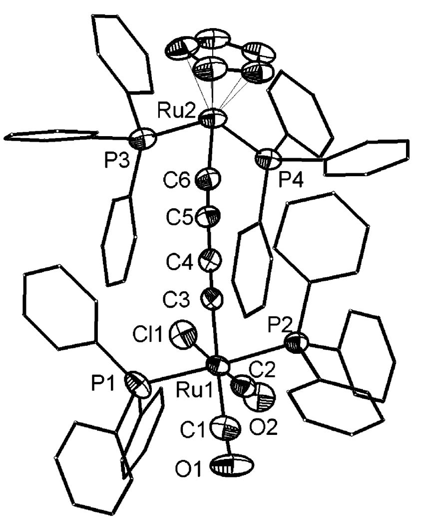


Figure 2. Molecular geometry of **5** in a crystal of **5**$\cdot 3C_6H_6$ (phenyl groups simplified, 50% displacement ellispsoids). Selected bond distances (Å) and angles (deg): Ru1−C2 = 1.864(5), Ru1−C1 = 1.927(6), Ru1−C3 = 2.065(4), Ru1−P2 = 2.4071(13), Ru1−P1 = 2.4112(14), Ru1−Cl1 = 2.4564(13), Ru2−C6 = 2.020(5), Ru2−P4 = 2.2824(14), Ru2−P3 = 2.2924(14), C3−C4 = 1.220(6), C4−C5 = 1.370(6), C5−C6 = 1.224(6); C6−Ru2−P4 = 85.16(13), C6−Ru2−P3 = 88.74(14), P4−Ru2−P3 = 102.85(5), C4−C3−Ru1 = 177.1(4), C3−C4−C5 = 178.8(5), C6−C5−C4 = 174.5(5), C5−C6−Ru2 = 176.0(4).

We have not yet succeeded in obtaining crystallographic grade crystals of **4**-PF_6; however, further support for its formulation is provided by the simple deprotonation reaction that is typical of vinylidenes of the form $[Ru({=}C{=}CHR)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ to provide the σ-alkynyls $[Ru(C{\equiv}CR)(PPh_3)_2(\eta\text{-}C_5H_5)]$.[17] Thus, treating a solution of **4**-PF_6 in THF with diethylamine provides the neutral bimetallic butadiynediyl complex $[Cl(CO)_2(Ph_3P)_2RuC{\equiv}CC{\equiv}CRu(PPh_3)_2(\eta\text{-}C_5H_5)]$ (**5**), the characterization of which included a crystallographic analysis.[18] Figure 2 depicts the molecular geometry of the bimetallic complex, while Table S1 (Supporting Information) collates structural data for the range of known 1,4-diruthenated butadiynes. All of these are symmetrically substituted, with identical ligand sets at either end comprising one $\eta^5\text{-}C_5R_5$ (R = H, Me) and two phosphine donors: i.e., strongly π-basic ruthenium termini. Complex **5** provides a rare opportunity to assess the effects of varying coligands while keeping the metal termini the same. Metal−alkynyl bonding is considered to include a modest π-retrodative component that appears maximized for octahedral d^6-metal centers devoid of competitive π-acidic co-ligands—a situation exemplified by the $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ terminus in **5**. In contrast,

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[14] The comparable conversion of $[OsCl\{C(H){=}S\}(CO)_2(PPh_3)_2]$ to $[OsCl\{{=}C(H)SCH_3\}(CO)_2(PPh_3)_2]^+$ is accompanied by an expected increase in mean ν_{CO} from 2010 to 2023 cm^{-1}: Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73.

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[18] **5**: diethylamine (1 mL) was added to a solution of **4**-PF_6 (0.10 g, 0.06 mmol) in THF (20 mL) and the mixture stirred for 20 min. Concentration under reduced pressure precipitated the lemon yellow product, which was recrystallized from CH_2Cl_2/EtOH as an ethanol monosolvate (analysis) or a benzene solvate from benzene (X-ray). Yield: 0.06 g (66%). IR (CH_2Cl_2): 2048, 1987 (ν_{CO}) cm^{-1}. IR (Nujol): 2044, 1983 (ν_{CO}) cm^{-1}. NMR (C_6D_6, 25 °C): ^1H, δ_H 4.43 (s, 5H, C_5H_5), 6.94, 7.04, 7.73, 8.36 (m × 4, 60 H, C_6H_5); $^{13}C\{^1H\}$, δ_C 80.3 (br, $C{\equiv}\mathit{C}Ru(Cp)$), 85.9 ($C_5H_5$), 95.7 (br, $(OC)Ru\mathit{C}{\equiv}C$), 102.1 ($(OC)RuC{\equiv}\mathit{C}$), 106.5 ($\mathit{C}{\equiv}CRu(Cp)$), the phenyl region was obscured by the solvent peak, no unambiguous assignments could be made, 192.1 (CO), 195.8 (CO); $^{31}P\{^1H\}$, δ_P 21.8, 51.3. ESI-MS: *m/z* 1461.7 $[M - Cl + NCMe]^+$, 1420.6 $[M - Cl]^+$. Anal. Found: C, 67.89; H, 4.89; N, 0.00. Calcd for $C_{83}H_{65}ClO_2P_4Ru_2\cdot EtOH$: C, 67.90; H, 4.76; N, 0.00. Crystal data for **5**$\cdot 3C_6H_6$: $C_{101}H_{83}ClO_2P_4Ru_2$, M_w = 1690.14, monoclinic, $P2_1/n$, $a = 13.189(3)$ Å, $b = 25.805(5)$ Å, $c = 24.164(5)$ Å, $\beta = 90.13(3)°$, $V = 8224(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.365$ Mg m^{-3}, $T = 200(2)$ K, yellow prisms, R1 = 0.064, wR2 = 0.151, for 14 527 independent, observed, absorption-corrected reflections ($I > 2\sigma(I)$, $2\theta_{max} = 44.30°$), 1084 parameters, CCDC 284088.

Ru1 is ligated by two strong π-acids, one of which interacts with both of the t_{2g}-type orbitals that might otherwise be exploited for retrodonation to the C_4 ligand. This is reflected in the significant (9σ) lengthening of Ru1−C3 relative to Ru2−C6, the former being the longest in Table S1. The cis $Ru1(CO)_2$ arrangement allows an internally referenced indication of the trans influence of the C_4 ligand relative to chloride. The Ru1−C1 bond is markedly (12σ) lengthened relative to Ru1−C2, possibly suggesting a degree of competitive π-acidity on the part of the C_4 ligand.

Acknowledgment. We are grateful to one reviewer for identifying an erroneous spectroscopic assignment of the $^{13}C\{^1H\}$ NMR data for **4**$^+$.

Supporting Information Available: Full details of the crystal structure determinations of **2**·C_6H_6 (CCDC 247962) and **5**·$3C_6H_6$ (CCDC 284088) in CIF format and Table S1, collating structural data for **5** and diruthenated butadiynes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050800O