Phosphaalkyne Hydrometalation: Synthesis and Reactivity of the Complexes [Ru(P═CHCMe$_3$)Cl(CA)(PPh$_3$)$_2$] (A = O, S)

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The reaction of [RuHCl(CO)(PPh$_3$)$_3$] (**1a**) with P≡CCMe$_3$ results in the formation of the phosphaalkenyl complex [Ru(P═CHCMe$_3$)Cl(CO)(PPh$_3$)$_2$] (**2a**). Being coordinatively unsaturated, **2a** reacts reversibly with CO to provide [Ru(P═CHCMe$_3$)Cl(CO)$_2$(PPh$_3$)$_2$] (**3**) and with isonitriles (CNR) to provide [Ru(P═CHCMe$_3$)Cl(CNR)(CO)(PPh$_3$)$_2$] [R = CMe$_3$ (**4a**), C$_6$H$_3$Me$_2$-2,6 (**4b**)]. With an excess of CNCMe$_3$, the salt [Ru(P═CHCMe$_3$)(CNR)$_2$(CO)(PPh$_3$)$_2$]-Cl **5**(Cl) is obtained. The anionic bidentate ligand K[H$_2$B(bta)$_2$] (bta = benzotriazolyl) reacts with **2a** via chloride displacement to provide [Ru(P═CHCMe$_3$){H$_2$B(bta)$_2$}(CO)(PPh$_3$)$_2$] (**6**) while the facially tridentate macrocycle 1,4,7-trithiacyclononane ([9]aneS$_3$) provides [Ru-(P═CHCMe$_3$)(CO)(PPh$_3$)([9]aneS$_3$)]Cl **7**(Cl). The thiocarbonyl complex [Ru{P═CHCMe$_3$)-Cl(CS)(PPh$_3$)$_2$] (**2b**), obtained from [RuHCl(CS)(PPh$_3$)$_3$] (**1b**) and P≡CCMe$_3$, reacts with [Et$_2$NH$_2$][S$_2$CNEt$_2$] or [9]aneS$_3$ to provide [Ru(P═CHCMe$_3$)(S$_2$CNEt$_2$)(CS)(PPh$_3$)$_2$] (**8**) and [Ru(P═CHCMe$_3$)(CS)(PPh$_3$)([9]aneS$_3$)]Cl **9**(Cl**)**, respectively. The salt **5**(Cl) or the neutral complex **4a** react slowly with air (accelerated by base), to provide the λ^5-phosphaalkenyl-metallacycle [Ru{P(═O)C(CMe$_3$)C(═O)}(CNCMe$_3$)$_2$(PPh$_3$)$_2$] (**10**). The reactions of **1a** with sodium formate or ferrocene carboxylate provides the complexes [Ru(P═CHCMe$_3$)(O$_2$CR)-(CO)(PPh$_3$)$_2$] (R = H (**11a**), C$_5$H$_4$Fe(η-C$_5$H$_5$) (**11b**)). The X-ray crystal structure of **11a** is reported.

Introduction

The coordination chemistry of phosphaalkynes has proven to be an extremely fertile area of growth in recent times.[1] Notwithstanding the simple coordination of phosphaalkynes to a metal center, by far the most intriguing aspect of this chemistry has been the many oligomerization processes which are effected by transition metals. In this respect, analogy is often made to superficially related transition metal mediated oligomerizations of alkynes. This viewpoint has considerable merit, although departures from the analogy are equally inspiring. Our own perspective on phosphaalkyne coordination chemistry is to pursue this analogy in the direction of other classical reactions of alkynes with metal centers. For example we have shown that alkyne metathesis by alkylidyne complexes finds parallel in phosphaalkyne chemistry.[2] This paper is concerned with the hydrometalation of phosphaalkynes by ruthenium hydrido complexes. The reactions of alkynes with hydride complexes of ruthenium or osmium typically proceeds via hydrometalation of the −C≡C− triple bond to provide σ-vinyl complexes,[3] although in recent times more complicated processes have been uncovered for terminal alkynes including the formation of alkynyl,[4] vinylidene,[5] alkylidene,[6] and alkylidyne complexes.[7]

We find that the hydroruthenation of phosphaalkynes does indeed proceed via simple and regioselective addition of the ruthenium hydride bond across the P≡C multiple bond to provide phosphaalkenyl complexes. Phosphaalkenyl complexes have been prepared previously;[8] however, it should be noted that in all prior cases the "P═CR$_2$" ligands bore either bulky kinetically stabilizing substituents (CR$_2$ = C(SiMe$_3$)$_2$, C(OSiMe$_3$)-C$_6$H$_2$Me$_3$-2,4,6) or π-dative thermodynamically stabilizing substituents (R = OSiMe$_3$, NMe$_2$). The present

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approach provides, for the first time, monosubstituted phosphaalkenyl ligands without recourse to such stabilization in addition to reassuringly supporting the alkyne/phosphaalkyne analogy. Aspects of this work have formed the basis of preliminary reports.[9,10] In the interim, it has been shown by Regitz that tin hydrides will also hydrometalate phosphaalkynes but with the opposite regiochemistry of addition across the P≡C multiple bond.[11]

Experimental Section

General Comments. All manipulations were routinely carried out under anaerobic conditions using conventional Schlenk tube and vacuum line techniques. However, none of the new compounds showed marked air-sensitivity during workup or subsequent spectroscopic characterization. Solvents were distilled from appropriate drying agents (ethers and parafins from Na/K alloy and benzophenone; dichloromethane from CaH_2) under an atmosphere of dry nitrogen and purged with nitrogen prior to use. The complexes $[RuHCl(CA)(PPh_3)_3]$ (A = O,[12] S[13]) and the compounds P≡CCMe$_3$[14] and K[H_2B(bta)$_2$][15] were prepared according to published procedures. All other reagents were used as received from commercial sources. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with a JEOL JNM EX270 NMR spectrometer and calibrated against internal $SiMe_4$ (^{1}H), internal $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P) references. "t^V" refers to virtual triplet resonances characteristic of a *trans*-Ru(PPh$_3$)$_2$ arrangement with apparent coupling constants being given. Infrared spectra were recorded both as dichloromethane solutions and Nujol mulls using Perkin-Elmer 1720-X or Mattson Series 1 FT-IR spectrometers. Characteristic "fingerprint" bands for PPh_3 are omitted. FAB-mass spectrometry was carried out using an Autospec Q instrument with 3-nitrobenzyl alcohol (nba) as a matrix. Compositional assignments are based on simulation of isotopic distributions; "M" refers to the molecular ion with the exception of salts for which it refers to the cationic complex. FAB-MS data are reported in the form *m*/*z* (% abundance) [assignment]. Elemental analysis was carried out by the Imperial College Microanalytical Service. In the case of analytical data for partial solvates, the stoichiometry was confirmed, where possible, by ^{1}H NMR integration.

Preparation of [Ru(P═CH^{t}Bu)Cl(CO)(PPh$_3$)$_2$] (2a). A solution of $[RuHCl(CO)(PPh_3)_3]$ (**1a**) (1.00 g, 1.05 mmol) in dichloromethane (50 mL) was treated with P≡CCMe$_3$ (0.43 mL) and stirred for 1 h during which time the solution turned bright orange. The solvent was removed and the residue washed with diethyl ether (2 × 10 mL) to remove PPh_3. The remaining solid was crystallized from a mixture of dichloromethane and diethyl ether. Yield: 0.76 g (92%). IR CH_2Cl_2: 1929 [ν(CO)] cm^{-1}; Nujol, 1929 sh, 1918 [ν(CO)], 1586, 1571, 1356, 1308, 1247, 863 cm^{-1}. NMR (CH_2Cl_2/$CDCl_3$, 25 °C): ^{1}H, δ 0.94 [s, 9 H, CH_3], 7.12 [dt, 1 H, P═CH, ^2J(PH) = 16.2, ^4J(P$_2$H) = 2.7 Hz], 7.42, 7.63 [m × 2, 30 H, C_6H_5] ppm; ^{13}C{^{1}H}, δ 202.4 [t, CO, ^2J(P$_2$C) = 15.2], 184.9 [d, P═C, ^1J(PC)= 58.9], 134.4 [t^v, C^{2,6} (C_6H_5), J(P$_2$C) = 5.4], 132.2 [t^v, C^1(C_6H_5), J(P$_2$C) = 22.3], 130.2 [s, C^4(C_6H_5)], 128.1 [t^v, C^{3,5}(C_6H_5), J(P$_2$C) = 5.4], 40.8 [d, CMe_3, ^2J(PC) = 10.7], 30.8 [d, CH_3, ^3J(PC) = 14.3 Hz] ppm; ^{31}P{^{1}H}, 450.4 [t, P═C, ^2J(P$_2$P) = 10.0], 33.9 [d, PPh_3, ^2J(P$_2$P) = 10.0 Hz] ppm. FAB-MS: *m*/*z* = 940 (64) [M + nba]$^+$, 791 (9) [M − H]$^+$, 689 (24) [HM − HPCHR]$^+$, 363 (32) [RuPPh$_3$]$^+$, 263 (100) [HPPh$_3$]$^+$. Anal. Found: C, 63.9; H, 5.6. Calcd for $C_{42}H_{40}ClOP_3Ru$: C, 63.8; H, 5.1. NB: The complex [Ru(P═CHAd)Cl(CO)(PPh$_3$)$_2$] (**2c**) (Ad = adamantyl) was observed from the reaction of **1a** with P≡C−Ad, however due to its high solubility, the complex was never adequately isolated free of PPh_3. ^{31}P{^{1}H}NMR: 457.7 [t, P═CH, J(P$_2$P) = 10.5], 34.2 [d, PPh_3, J(P$_2$P) = 10.5 Hz]. No reaction was observed between **1a** and the sterically cumbersome P≡CC_6H_2^{t}Bu$_3$-2,4,6.

Preparation of [Ru(P═CHCMe$_3$)Cl(CS)(PPh$_3$)$_2$] (2b). A solution of $[RuHCl(CS)(PPh_3)_3]$ (1.00 g, 1.03 mmol) in dichloromethane (50 mL) was treated with P≡CCMe$_3$ (0.43 mL, ca. 2.3 equiv) and stirred for 1 h and the mixture then freed of volatiles in vacuo. The residue was dissolved in dichloromethane (50 mL) and diethyl ether (60 mL) added. Slow reduction in solvent volume provided crystals of the orange product, which were washed with diethyl ether (20 mL), hexane (20 mL), and dried in vacuo. Yield: 0.74 g (89%). IR CH_2Cl_2: 1280 [ν(CS)] cm^{-1}; Nujol, 1586, 1571, 1267 [ν(CS)], 1246, 919, 861, 845 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 0.99 [s, 9 H, CH_3], 7.35−7.71 [m, 31 H, C_6H_5 + P═CH] ppm; ^{13}C{^{1}H} (CH_2Cl_2/$CDCl_3$, 25 °C), δ 297.7 [t, CS, ^2J(P$_2$C) = 15.2], 183.2 [d, P═C, ^1J(PC)= 57.1], 134.7 [t^v, C^{2,6}(C_6H_5), J(P$_2$C) = 5.3], 131.2 [t^v, C^1(C_6H_5), J(P$_2$C) = 23.2], 130.2 [s, C^4(C_6H_5)], 128.0 [t^v, C^{3,5}(C_6H_5), J(P$_2$C) = 5.4], 41.0 [d, CMe_3, ^2J(PC) = 9.0], 31.0 [d, CH_3, ^3J(PC) = 12.5 Hz] ppm; ^{31}P{^{1}H}, 445.2 [t, P═C, ^2J(P$_2$P) = 12.3], 33.3 [d, PPh_3, ^2J(P$_2$P) = 12.2 Hz] ppm. FAB-MS: *m*/*z* 956 (39) [M + nba]$^+$, 705 (5) [HM − HPCHR]$^+$, 694 (19) [M + nba − PPh$_3$]$^+$, 670 (21) [HM − Cl − HPCHR]$^+$. Anal. Found: C, 62.4; H, 5.1. Calcd for $C_{42}H_{40}ClP_3RuS$: C, 62.6; H, 5.0.

Preparation of [Ru(P═CH^{t}Bu)Cl(CO)$_2$(PPh$_3$)$_2$] (3). Carbon monoxide was passed through a solution of [Ru(P═CH^{t}Bu)Cl(CO)(PPh$_3$)$_2$] (**2a**; 0.15 g, 0.19 mmol) in dichloromethane (4 mL) for 2 min. Diethyl ether (20 mL) was added and the mixture cooled to −10 °C for 12 h to provide pale yellow crystals. Yield: 0.13 g (84%). The compound must be stored under an atmosphere of carbon monoxide due to very facile decarbonylation. For this reason satisfactory elemental microanalytical data were not obtained. IR CH_2Cl_2: 2023, 1969 [ν(CO)] cm^{-1}; Nujol, 2024, 1975, 1256, 1096sh, 1090, 861 cm^{-1}. NMR (CD_2Cl_2, 25 °C): ^{1}H, δ 0.87 [s, 9 H, CH_3], 7.39, 7.88 [m × 2, 30 H, C_6H_5], 8.03 [d, 1 H, P═CH, ^2J(PH) = 18.9 Hz] ppm; ^{13}C{^{1}H}, δ 198.7, 193.0 [t (br) × 2, RuCO, ^2J(PC) not resolved], 196.8 [d, P═C, ^1J(PC)= 62.5 Hz], 134.2 [t^v, C^{2,6}(C_6H_5)], 133.1 [t^v, C^1(C_6H_5), J(P$_2$C) = 26.8], 130.1 [s, C^4(C_6H_5)], 128.0 [t^v, C^{3,5}-(C_6H_5), J(P$_2$C) = 5.4], 41.8 [d(br), *C*Me$_3$, ^2J(PC) not resolved], 30.4 [d, CH_3, ^3J(PC) = 12.5 Hz] ppm; ^{31}P{^{1}H}, 369.5 [s (br), P═C, ^2J(P$_2$P) not resolved], 22.1 [s(br), PPh_3] ppm. FAB-MS: *m*/*z* = 940 (41) [M − CO + nba]$^+$, 819 (18) [M]$^+$, 789 (2) [M − H − CO]$^+$, 689 (24) [M − HP═CHR − CO]$^+$, 363 (24) [RuPPh$_3$]$^+$, 263 [HPPh$_3$]$^+$.

Preparation of [Ru(P═CHCMe$_3$)Cl(CN^{t}Bu)(CO)(PPh$_3$)$_2$] (4a). [Ru(P═CH^{t}Bu)Cl(CO)(PPh$_3$)$_2$] (**2a**; 0.10 g, 0.13 mmol) was suspended in diethyl ether (25 mL) and pivalo isocyanide (CNCMe$_3$, 0.015 mL, 0.011 g, 0.13 mmol) added. The reaction was stirred for 30 min and the yellow precipitate filtered off, washed with diethyl ether (10 mL), hexane (10 mL), and dried in vacuo. Yield: 0.10 g (91%). The product can be recrystallized from mixtures of dichloromethane and ethanol. IR CH_2Cl_2: 2148 [ν(CN)], 1961 [ν(CO)] cm^{-1}; Nujol, 2148 [ν(CN)], 1930 [ν(CO)], 1587, 1571, 1311, 1240, 1201, 968, 890, 862 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 0.79 [s, 9 H, CH_3], 0.97 [s, 9 H, CH_3], 7.29−7.95 [m, 31 H, C_6H_5 and P═CH] ppm; ^{31}P{^{1}H}, 389.8 [t, P═C, J(P$_2$P) = 11.7], 24.6 [d, PPh_3, J(P$_2$P) = 11.7 Hz] ppm. FAB-MS: *m*/*z* = 953 (14) [M + CN^{t}Bu]$^+$, 874 (5) [M]$^+$, 844 (1) [M − CO]$^+$, 789 (2) [M − CN^{t}Bu]$^+$, 772 (15) [HM − HPCHR]$^+$, 744 (10) [HM − CO − HPCHR]$^+$, 709 (11) [Ru-

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$(CN^tBu)(PPh_3)_2]^+$, 689 (3) $[RuCl(CO)(PPh_3)_2]^+$, 654 (6) $[Ru(CO)(PPh_3)_2]^+$, 625 (6) $[Ru(PPh_3)_2]^+$, 363 (22) $[RuPPh_3]^+$. Anal. Found: C, 62.2; H, 5.3; N, 1.5. Calcd for $C_{47}H_{49}ClNOP_3Ru\cdot 0.5CH_2Cl_2$: C, 62.3; H, 5.5; N, 1.5.

Preparation of [Ru(P=CHCMe$_3$)Cl(CNC$_6$H$_3$Me$_2$-2,6)(CO)(PPh$_3$)$_2$] (4b). $[Ru(P{=}CH^tBu)Cl(CO)(PPh_3)_2]$ (**2a**, 0.15 g, 0.19 mmol) was dissolved in dichloromethane (5 mL) and 2,6-dimethylphenyl isocyanide (0.030 g, 0.23 mmol) added. The reaction was stirred for 5 min and then freed of volatiles in vacuo. The residue was crystallized from a mixture of dichloromethane and diethyl ether, washed with diethyl ether (10 mL), and dried in vacuo. Yield: 0.12 g (69%). IR CH_2Cl_2: 2109 [ν(CN)], 1960 [ν(CO)] cm^{-1}; Nujol, 2121, 2111sh [ν(CN)], 1962 [ν(CO)], 1586, 1573, 1314, 1250, 863 cm^{-1}. NMR (CD_2Cl_2, 25 °C): ^{1}H, δ 0.85 [s, 9 H, C(CH$_3$)$_3$], 2.08 [s, 6 H, C$_6$H$_3$(CH$_3$)$_2$], 6.96 [d, 2 H, H^{3,5}(C$_6$H$_3$)], 7.05 [t, 1 H, H^4(C$_6$H$_3$), J(HH) = 6.9 Hz], 7.27, 7.80 [m × 2, 30 H, C$_6$H$_5$], 8.11 [dt, 1 H, P=CH, ^2J(PH) = 19.2 Hz, ^4J(PP) discernible but not resolved] ppm; ^{13}C{^{1}H}, 200.8 [t, RuCO, ^2J(P$_2$C) = 12.5], 195.1 [dt, P=CH, ^2J(PC) = 64.2, ^3J(P$_2$C) = ca. 4.5], 161 [br, CNR], 134.31 [t^v, C^1(C$_6$H$_5$), J(P$_2$C) = 17.0], 134.27 [t^v, C^{2,6}(C$_6$H$_5$), J(PC) not resolved], 129.5 [s, C^4(C$_6$H$_5$)], 127.9 [C^{3,5}(C$_6$H$_3$)], 127.5 [t^v, C^{3,5}(C$_6$H$_5$), J(P$_2$C) = 5.4], 41.8 [d, CMe$_3$, ^2J(PC) = 12.5], 30.5 [d, (CH$_3$)$_3$, ^3J(PC) = 14.3 Hz], 18.3 [C$_6$H$_3$CH$_3$] ppm; ^{31}P{^{1}H}, 391.0 [t, P=C, J(P$_2$P) = 11.1], 24.4 [d, PPh$_3$, J(P$_2$P) = 10.2 Hz] ppm. FAB-MS: m/z = 1075 (3) [HM + nba]$^+$, 940 (13) [HM + H$_2$O], 922 (42) [HM]$^+$, 820 (92) [HM − HPCHR]$^+$, 792 (72) [HM − HP=CHR − CO]$^+$, 757 (15) [HM − HP=CHR − CO − Cl]$^+$, 558 (33) [M − HP=CHR − PPh$_3$]$^+$, 523 (8) [M − HP=CHR − PPh$_3$ − Cl]$^+$, 494 (41) [M − HP=CHR − PPh$_3$ − Cl − CO]$^+$, 363 (78) [RuPPh$_3$]$^+$, 263 (100) [HPPh$_3$]$^+$. Anal. Found: C, 65.0 H, 5.7; N, 1.5. Calcd for $C_{51}H_{49}ClNOP_3Ru\cdot H_2O$: C, 65.2; H, 5.5; N, 1.5.

Preparation of [Ru(P=CH^{t}Bu)(CN^{t}Bu)$_2$(CO)(PPh$_3$)$_2$]Cl 5(Cl). A solution of $[Ru(P{=}CH^tBu)Cl(CO)(PPh_3)_2]$ (**2a**; 0.20 g, 0.25 mmol) in dichloromethane (15 mL) was treated with pivalo isocyanide (0.06 mL, 0.04 g, 0.53 mmol). The mixture was stirred for 2 h, and then all solvent was removed in vacuo. A cream solid was then obtained by ultrasonic trituration of the residue in hexane (15 mL). This product was washed with hexane (10 mL) and dried in vacuo. Yield: 0.21 g (95%). The salt could be recrystallized from a mixture of dichloromethane and ethanol. IR CH_2Cl_2: 2179, 2156 [ν(CN)], 2021 [ν(CO)] cm^{-1}; Nujol, 2184, 2163 [ν(CN)], 2003, 1980 [ν(CO)], 1720, 1627, 1311, 1234, 1187, 931, 862, 846 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 0.66 [s, 9 H, NCCH$_3$], 0.96 [s, 9 H, PCCH$_3$], 1.18 [s, 9 H, NCCH$_3$], 7.32−7.77 [m, 31 H, PC$_6$H$_5$ + P=CH] ppm; ^{31}P{^{1}H}, 336.8 [s, P=C], 33.5 [s, PPh$_3$] ppm. FAB-MS: m/z = 921 (34) [M]$^+$, 838 (100) [M − CN^{t}Bu]$^+$, 810 (16) [M − CO − CN^{t}Bu]$^+$, 792 (10) [HM − CO − HPCHR]$^+$, 735 (3) [HM − CN^{t}Bu − HPCHR]$^+$, 708 (14) [HM − CN^{t}Bu − CO − HPCHR]$^+$, 576 (2) [M − PPh$_3$]$^+$, 547 (8) [M − CO − PPh$_3$]$^+$, 530 (26) [M − CN^{t}Bu-PPh$_3$]$^+$, 363 (29) [RuPPh$_3$]$^+$. Anal. Found: C, 60.0; H, 5.0; N, 2.6. Calcd for $C_{52}H_{58}ClN_2OP_3Ru\cdot 1.5CH_2Cl_2$: C, 59.9; H, 5.7; N, 2.6.

Preparation of [Ru(P=CH^{t}Bu)(CN^{t}Bu)$_2$(CO)(PPh$_3$)$_2$]-O$_2$CH 5(O$_2$CH). $[Ru(P{=}CH^tBu)(O_2CH)(CO)(PPh_3)_2]$ (**11a**; 0.10 g, 0.13 mmol) was dissolved in dichloromethane (10 mL) and CNCMe$_3$ (0.1 mL, excess) added. The mixture was stirred for 30 min leading to a decolorization of the orange-yellow solution. All solvent was removed and diethyl ether (20 mL) added. Trituration in an ultrasound bath provided a colorless solid which was filtered off, washed with diethyl ether (20 mL) and hexane (20 mL), and dried in vacuo. Yield: 0.09 g (75%). The salt was characterized by comparison of spectroscopic data with those described above for **5**(Cl).

Preparation of [Ru(P=CH^{t}Bu){H$_2$B(bta)$_2$}(CO)(PPh$_3$)$_2$] (6). $[Ru(P{=}CH^tBu)Cl(CO)(PPh_3)_3]$ (**2a**; 0.15 g, 0.19 mmol) and K[H$_2$B(bta)$_2$] (0.06 g, 0.21 mmol) were degassed in vacuo and then dissolved in degassed dichloromethane (5 mL) and acetone (1 mL). The solution was stirred for 30 min after an initial color change to yellow. Filtration through diatomaceous earth was followed by evaporation of the solvent from the filtrate under reduced pressure. The crude product was triturated in diethyl ether (10 mL) in an ultrasound bath to provide a pale yellow solid, which was filtered off, washed with diethyl ether (5 mL), and dried in vacuo. Yield: 0.08 g (42%). The product can be recrystallized from dichloromethane and diethyl ether. IR (Nujol): 2435, 2418 [ν(BH$_2$)], 1959 [ν(CO)], 1295, 1273, 1241, 1190, 1147, 1133, 1104, 1075, 934, 868, 844 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 0.81 [s, 9 H, CH$_3$], 3.45 [s (br), 2 H, BH$_2$], 6.9−8.0 [m, 39 H, C$_6$H$_5$, C$_6$H$_4$ + P=CH] ppm; ^{31}P{^{1}H}, 391.0 [s, P=C], 28.9 [s, PPh$_3$] ppm. FAB-MS: m/z = 1005 (12) [M + 2H]$^+$, 743 (25) [M + 2H − PPh$_3$]$^+$, 655 (52) [HM − HPCHR − H$_2$B(bta)$_2$]$^+$, 625 (27) $[Ru(PPh_3)_2]^+$, 363 (42) $[RuPPh_3]^+$. Anal. Found: C, 56.8; H, 4.6; N, 7.6. Calcd for $C_{54}H_{50}BN_6P_3ORu\cdot 2CH_2Cl_2$: C, 57.3; H, 4.6; N, 7.2.

Preparation of [Ru(P=CH^{t}Bu)(CO)(PPh$_3$)([9]aneS$_3$)]Cl 7(Cl). $[Ru(P{=}CH^tBu)Cl(CO)(PPh_3)_2]$ (**2a**; 0.22 g, 0.28 mmol) and [9]aneS$_3$ (0.06 g, 0.33 mmol) were degassed under vacuum and dissolved in dry, degassed dichloromethane (10 mL). After being stirred for 20 h under nitrogen, the solution was taken to dryness in vacuo. The resulting yellow oil was triturated ultrasonically in diethyl ether (15 mL) to provide cream crystals. These were washed with diethyl ether (10 mL), petroleum ether (10 mL), and dried. Yield: 0.12 g (61%). The product can be recrystallized from mixtures of dichloromethane and diethyl ether. IR (Nujol): 1977 [ν(CO)], 1717, 1636, 1310, 1270, 1234, 943, 912, 884, 824 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, 1.02 [s, 9 H, CH$_3$], 1.6, 2.1, 2.4, 2.8, 3.4, 3.6, 3.9 [m × 7, 12 H, SCH$_2$], 7.45 [m, 15 H, C$_6$H$_5$], 8.94 [d, 1 H, P=CH, J(PH) = 18.8 Hz] ppm; ^{13}C{^{1}H}, 204.5 [d, P=C, ^1J(PC) = 64.3], 200.0 [d, CO, ^2J(PC) = 16.0], 134.2 [d, C^{2,6}(C$_6$H$_5$), ^2J(PC) = 10.8], 132.5 [d, C^1(C$_6$H$_5$), ^1J(PC) = 46.4], 131.4 [s, C^4(C$_6$H$_5$)], 129.1 [d, C^{3,5}(C$_6$H$_5$), ^3J(PC) = 10.7], 52.8 [d, SCH$_2$, ^3J(PC) = 35.7], 43.2 [d, P=C*C*, ^2J(PC) = 10.7], 38.2, 35.9, 34.7 [SCH$_2$], 31.2 [d, SCH$_2$, ^3J(PC) 42.8 Hz], 31.1[CH$_3$] ppm; ^{31}P{^{1}H}, 357.5 [P=C], 37.7 [PPh$_3$] ppm. FAB-MS: m/z = 691 (100) [M + H$_2$O]$^+$, 571 (4) [HM − HPCHR]$^+$, 516 (6) [HM − HPCHR − 2C$_2$H$_4$]$^+$. Anal. Found for **7**(PF$_6$): C, 40.9; H, 4.3. Calcd for $C_{30}H_{37}F_6P_3RuS_4\cdot CH_2Cl_2$: C, 40.5; H, 4.3.

Preparation of [Ru(P=CH^{t}Bu)(S$_2$CNEt$_2$)(CS)(PPh$_3$)$_2$] (8). $[Ru(P{=}C^tBu)Cl(CS)(PPh_3)_2]$ (**2b**; 0.15 g, 0.19 mmol) and [Et$_2$NH$_2$][S$_2$CNEt$_2$] (0.05 g, 0.23 mmol) were degassed in vacuo and dissolved in dry, degassed dichloromethane (10 mL). An immediate color change from orange to yellow was observed. After 40 min of stirring, the solvent volume was reduced in vacuo and dry, degassed ethanol (40 mL) added slowly to precipitate the bright yellow product. This was filtered off, washed with ethanol (10 mL) and petroleum ether (10 mL), and dried in vacuo. Yield: 0.09 g (53%). The complex could be recrystallized from a mixture of dichloromethane and hexane. IR (Nujol): 1585, 1572, 1358, 1252 [ν(CS)], 1214, 917, 809, 849 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 0.81 [s, 9 H, CH$_3$], 1.2, 1.8 [m × 2, 6 H, NCCH$_3$], 2.72, 3.02 [m × 2, 4 H, CH$_2$], 7.31, 7.68 [m × 2, 30 H, C$_6$H$_5$], 7.89 [d, 1 H, P=CH] ppm; ^{13}C{^{1}H}, δ 305.4 [dt, CS, J(P$_2$C) ≈ J(PC) = 12.7], 202.7 [d, S$_2$C, ^3J(PC) = 23.2], 190.0 [d, P=C, J(PC) = 62.5], 135.2 [t^v, C^{2,6}(C$_6$H$_5$), J(P$_2$C) = 5.4], 133.9 [t^v, C^1(C$_6$H$_5$), J(P$_2$C) = 18.8], 128.9 [s, C^4(C$_6$H$_5$)], 127.1 [t^v, C^{3,5}(C$_6$H$_5$), J(P$_2$C) = 5.4], 43.8, 43.4 [s x 2, CH$_2$], 43.6 [d, PCMe$_3$, J(PC) unresolved], 31.1 [d, PCC*C*H$_3$, J(PC) = 12.5 Hz], 30.6, 30.5 [s x 2, 2 x NC*C*H$_3$] ppm; ^{31}P{^{1}H}, 387.6 [s, P=C], 35.5 [s, PPh$_3$] ppm. FAB-MS: m/z = 919 (20) [M]$^+$, 818 (6) [HM − HPCHR]$^+$, 658 (100) [M − PPh$_3$]$^+$, 556 (40) [HM − HPCHR − PPh$_3$]$^+$. Anal. Found: C, 59.8; H, 5.3; N, 1.6. Calcd for $C_{47}H_{50}Cl_2NP_3Ru_2S_3$: C, 60.0; H, 5.4; N, 1.5.

Preparation of [Ru(P=CH^{t}Bu)(CS)(PPh$_3$)([9]aneS$_3$)]Cl 9(Cl). $[Ru(P{=}CH^tBu)Cl(CS)(PPh_3)_2]$ (**2b**; 0.20 g, 0.25 mmol) and [9]aneS$_3$ (0.05 g, 0.28 mmol) were degassed in vacuo and then dissolved in dry, degassed dichloromethane (10 mL), and the mixture was stirred for 18 h under nitrogen. All solvent

was removed in vacuo and the residual yellow oil triturated ultrasonically in diethyl ether (15 mL) to provide an off-white product. This was washed with diethyl ether (10 mL) and hexane (10 mL) and dried in vacuo. Yield: 0.10 g (55%). The salt could be recrystallized from a mixture of dichloromethane and hexane. IR (Nujol): 1621, 1299, 1284 [ν(CS)], 1018, 941 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H, δ 0.80−1.49, 2.10−3.75 [m × 2, 12 H, SCH_2], 0.99 [s, 9 H, CH_3], 7.42−7.60 [m, 30 H, C_6H_5], 8.99 [d, 1 H, P═CH, ^2J(HP) not resolved] ppm; $^{31}P\{^1H\}$, 353.5 [s, P═CH], 36.3 [s, PPh_3] ppm. FAB-MS: *m/z* 689 (4) $[M]^+$, 631 (6) $[M - 2C_2H_4]^+$, 588 (1) $[HM - HPCHR]^+$. Anal. Found for **9**(PF_6): C, 40.6; H, 4.2. Calcd for $C_{30}H_{37}F_6OP_3RuS_4 \cdot CH_2Cl_2$: C, 40.6; H, 4.3.

Preparation of [Ru{κ^2-C(═O)C(^{t}Bu)═P═O}($CN^tBu)_2$($PPh_3)_2$] (10). [Ru(P═CH^{t}Bu)($CN^tBu)_2$(CO)($PPh_3)_2$]Cl (**5**(Cl); 0.10 g, 0.11 mmol) was dissolved in a mixture of dichloromethane (15 mL) and ethanol (5 mL) and stirred under air with an excess of $CNCMe_3$ (0.1 mL) for 5 d. All solvent and excess $CNCMe_3$ was removed in vacuo and the resulting oil triturated ultrasonically in diethyl ether (15 mL). The colorless product obtained was washed with diethyl ether (10 mL) and hexane (10 mL) and dried in vacuo. Yield: 0.08 g (82%). The product can be recrystallized from chloroform−ethanol mixtures. IR CH_2Cl_2: 2171, 2038 [ν(CN)], 1644 [ν(C═O)] cm^{-1}; Nujol, 2169, 2028 [ν(CN)], 1644 [ν(C═O)], 1234, 1189 [ν(PO)], 921, 890, 846 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H, δ 0.61 [s, 9 H, $NCCH_3$], 0.87 [s, 9 H, $PCCH_3$], 1.27 [s, 9 H, $NCCH_3$], 7.28−7.73 [m, 30 H, PC_6H_5] ppm; $^{31}P\{^1H\}$, 47.0 [t, P═O, $^2J(P_2P)$ = 25.2], 31.2 [d, PPh_3, $^2J(PP_2)$ = 25.2 Hz] ppm. FAB-MS: *m/z* = 856 (2) $[M - CN^tBu]^+$, 530 (2) $[M - OPCRCO - PPh_3]^+$. Anal. Found: C, 59.4; H, 5.4; N, 3.2. Calcd for $C_{52}H_{57}N_2O_2P_3Ru \cdot 1.75CH_2Cl_2$: C, 59.5; H, 5.6; N, 2.6. The complex was also characterized crystallographically.[10]

Preparation of [Ru(P═CH^{t}Bu)(O_2CH)(CO)($PPh_3)_2$] (11a). [Ru(P═CH^{t}Bu)Cl(CO)($PPh_3)_2$] (**2a**; 0.10 g, 0.13 mmol) was dissolved in dichloromethane (20 mL) and ethanol (10 mL). Sodium formate (0.02 g, 0.44 mmol) dissolved in water (1 mL) and ethanol (10 mL) was added and the mixture stirred for 5 min. The solvent volume was slowly reduced by rotary evaporation resulting in formation of an orange microcrystalline product. This was washed with ethanol (20 mL) and hexane (20 mL) and dried in vacuo. Yield: 0.09 g (87%). IR: Nujol, 1922 [ν(CO)], 1554 [$\nu(CO_2)$], 1309, 1249, 1186, 970, 937, 863, 800 cm^{-1}; CH_2Cl_2, 1924 [ν(CO)], 1552 [$\nu(CO_2)$] cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H, δ 0.66 [s, 9 H, CH_3], 6.88 [dt, 1 H, O_2CH, J(HP) = 1.32 Hz, $J(HP_2)$ not resolved], 7.3−7.5 [m, 31 H, PC_6H_5 + P═CH] ppm; $^{13}C\{^1H\}$, δ 205.7 [t, CO, $J(P_2C)$ = 15.8], 187.4 [dt, P═C, ^1J(PC) = 59.2, $^3J(P_2C)$ = 3.8], 171.3 [O_2C], 134.5 [t^v, $C^{2,6}(C_6H_5)$, $J(P_2C)$ = 5.4], 131.4 [t^v, $C^1(C_6H_5)$, $J(P_2C)$ = 22.3], 130.1 [s, $C^4(C_6H_5)$], 128.1 [t^v, $C^{3,5}(C_6H_5)$, $J(P_2C)$ = 6.6], 41.1 [d, *C*Me_3, J(PC) 10.0], 31.2 [d, CH_3, J(PC) = 13.1 Hz], ppm; $^{31}P\{^1H\}$, 426.5 [t, P═CH, $J(P_2P)$ = 8.0], 38.5 [d, PPh_3, $J(P_2P)$ = 10.0 Hz] ppm. FAB-MS: *m/z* (%) = 800 (11) $[M]^+$, 755 (14) $[M - O_2CH]^+$, 727 (2) $[M - CO - O_2CH]^+$, 701 (30) $[M - HPCHR]^+$, 671 (12) $[M - CO - HPCHR]^+$, 654 (65) $[M - O_2CH - HPCHR]^+$, 626 (33) $[M - CO - O_2CH - HPCHR]^+$, 363 (50) $[RuPPh_3]^+$. Anal. Found: C, 61.9; H, 5.2. Calcd for $C_{43}H_{41}O_3P_3Ru \cdot 0.5CH_2Cl_2$: C, 62.0; H, 5.0. Crystals obtained from a mixture of chloroform and diethyl ether were characterized crystallographically (vide infra).

Preparation of [Ru(P═CH^{t}Bu){$O_2CC_5H_4FeC_5H_5$}(CO)($PPh_3)_2$] (11b). [Ru(P═CH^{t}Bu)Cl(CO)($PPh_3)_2$] (**2a**; 0.10 g, 0.13 mmol) was dissolved in dichloromethane (20 mL) and ethanol (10 mL). To this was added an ethanolic solution (5 mL) of ferrocenecarboxylate sodium salt (prepared by the reaction of ferrocenecarboxylic acid with aqueous sodium hydroxide, 0.05 g, 0.20 mmol) and the mixture stirred for 5 min. The solvent volume was reduced by rotary evaporation to precipitate an orange product. This was redissolved in dichloromethane and filtered through diatomaceous earth. Ethanol was added and the product precipitated by rotary evaporation. This was washed with ethanol (10 mL) and hexane (10 mL) and dried in vacuo. Yield: 0.08 g (64%). The product can be recrystallized from chloroform−ethanol mixtures. IR: Nujol, 1926 [ν(CO)], 1585, 1571, 1311, 1249, 1107, 863, 809, 771 cm^{-1}; CH_2Cl_2, 1920 [ν(CO)], 1646 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H, δ 0.62 [s, 9 H, CH_3], 3.43 [s, 5 H, C_5H_5], 3.78, 3.94 [t x 2, 4 H, C_5H_4, J(HH) = 1.87 Hz], 7.3−7.8 [m, 31 H, PC_6H_5 + PCH] ppm; $^{31}P\{^1H\}$, 419.7 [s(br), PCH], 36.7 [d, PPh_3, J(PP) = 8.0 Hz] ppm. FAB-MS: *m/z* (%) [Fc = ferrocenyl] = 984 (25) $[M]^+$, 956 (3) $[M - CO]^+$, 883 (36) $[M - HPCHR]^+$, 755 (45) $[M - FcCO_2]^+$, 722 (100) $[M - PPh_3]^+$, 694 (32) $[M - PPh_3 - CO]^+$, 655 (51) $[M - FcCO_2 - HPCHR]^+$, 625 (82) $[Ru(PPh_3)_2]^+$, 363 (86) $[RuPPh_3]^+$, 263 (68) $[HPPh_3]^+$. Anal. Found: C, 51.2; H, 4.1. $C_{53}H_{49}FeO_3P_3Ru \cdot 2.75CHCl_3$: C, 51.0; H, 4.0.

Crystal Structure Determination of [Ru(P═CH^{t}Bu)(O_2CH)(CO)($PPh_3)_2$] (11a). A summary of the crystal data, data collection, and refinement details is given in Table 1. The structure was solved by direct methods, and all the major occupancy non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 to give R_1= 0.058, and wR_2 = 0.143 for 5114 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 120°$] and 427 parameters. Phenyl rings were refined as optimized rigid bodies. Hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, U(H) = 1.2U_{eq}(C) [U(H) = 1.5U_{eq}(*C*-Me)], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system (version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Selected bond lengths and angles are given in Table 2.

Table 1. Crystal Data and Data Collection and Solution and Refinement Details for [Ru(P═CHCMe$_3$)(O_2CH)(CO)($PPh_3)_2$] (11a)

Crystal Data	
emp formula	$C_{43}H_{41}O_3P_3Ru \cdot CHCl_3$
M_r	919.1
$a-c$ (Å)	10.002(1), 12.219(1), 19.580(1)
$\alpha-\gamma$ (deg)	88.55(1), 84.71(1), 67.28(1)
V (Å^3)	2197.9(2)
space grp	$P\bar{1}$
Z	2
D_{calcd} (g cm^{-3})	1.389
cryst size (mm)	0.40 × 0.17 × 0.10
Data Collection	
T (K)	293
diffractometer	Siemens P4/PC
wavelength	Cu Kα, 1.541 78 Å
scan type	ω-scans ($4.54 \le 2\theta \le 120.0°$)
abs cor; max, min transm	ellipsoidal; 0.67, 0.43
no. of data	6504 unique; 5114 with $F \ge 4\sigma(F)$ retained
Solution and Refinement	
method	direct and difference Fourier
program	SHELXTL PC, version 5.03
residuals	R_1 = 0.058, wR_2 = 0.143 (427 parameters)
	e density max = 0.88, min = −1.06 e Å^{-3}

Results and Discussion

The complex [RuHCl(CO)($PPh_3)_3$] (**1a**) reacts readily with alkynes[16] and diynes[17] to provide alkenyl or enynyl complexes (Scheme 1). While the precursor is coordinatively saturated, the replacement of the hydride

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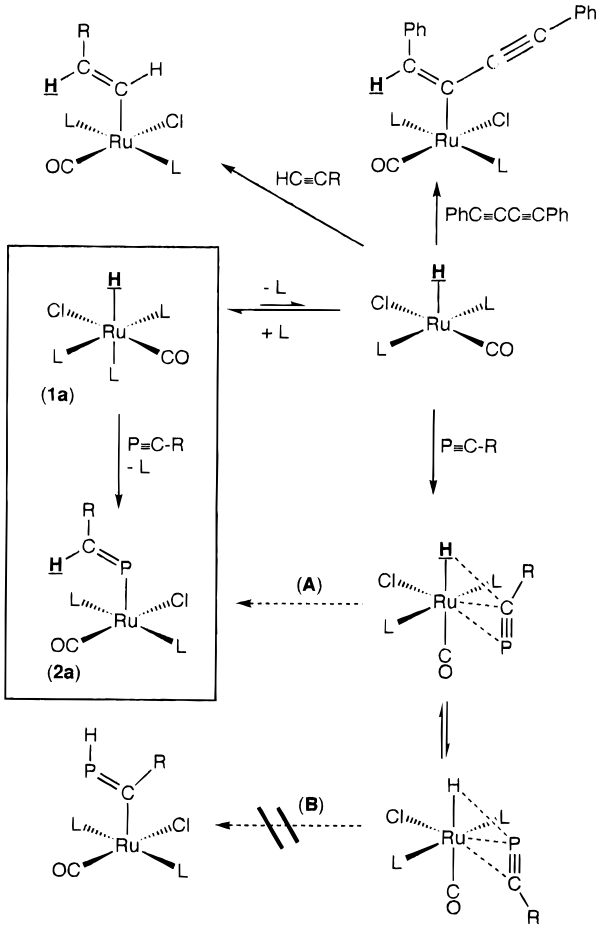
(17) Hill, A. F.; Melling, R. P. *J. Organomet. Chem.* **1990**, *396*, C22. Hill, A. F.; Melling, R. P.; Thompsett, A. R. *J. Organomet. Chem.* **1991**, *402*, C8. Hill, A. F.; Harris, M. C. J.; Melling, R. P. *Polyhedron* **1992**, *11*, 781.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 11a

Ru−C	1.808(6)	Ru−P(1)	2.295(2)
Ru−O(6)	2.366(5)	Ru−O(8)	2.182(5)
Ru−P(2)	2.378(2)	Ru−P(3)	2.386(2)
P(1)−C(1)	1.640(8)	C−O	1.135(8)
C(1)−C(2)	1.522(9)	C(7)−O(6)	1.237(9)
C(7)−O(8)	1.241(9)		
C−Ru−O(8)	174.2(2)	C−Ru−P(1)	94.5(2)
O(8)−Ru-P(1)	91.3(1)	C−Ru−O(6)	117.1(2)
O(8)−Ru-O(6)	57.1(2)	P(1)−Ru-O(6)	148.4(1)
C−Ru−P(2)	89.4(2)	O(8)−Ru-P(2)	90.5(1)
P(1)−Ru-P(2)	93.2(1)	O(6)−Ru-P(2)	86.2(2)
C−Ru−P(3)	90.6(2)	O(8)−Ru-P(3)	89.0(1)
P(1)−Ru-P(3)	92.0(1)	O(6)−Ru-P(3)	89.2(2)
P(2)−Ru-P(3)	174.8(1)	C(1)−P(1)-Ru	119.1(3)
Ru−C−O	177.5(6)	P(1)−C(1)-C(2)	127.4(7)
Ru−O(6)−C(7)	85.6(4)	Ru−O(8)−C(7)	94.0(4)
O(6)−C(7)-O(8)	123.3(6)		

Scheme 1[a]



[a] L = PPh_3 and R = CMe_3.

ligand by a σ-organyl group disfavors the recoordination of the labile phosphine originally present. The resulting 16-electron complexes enter into ligand addition and substitution reactions with a wide range of ligands including CO,[18] isocyanides,[17,19] poly(azolyl) chelates,[20] scorpionates,[21] sulfur-based macrocycles,[22] triboronates,[23] dithiocarbamates,[24] and phosphonio dithiocarboxylates.[25] The complex **1a** therefore appeared an ideal substrate for investigating the potential hydrometalation of phosphaalkynes, both from the point of view of facility and the synthetic potential of the anticipated product. A reaction rapidly ensues at room temperature in dichloromethane between **1a** and P≡$CCMe_3$ to provide a red solution from which a complex formulated as [Ru(P═$CHCMe_3$)Cl(CO)(PPh_3)$_2$] (**2a**) may be isolated in 92% yield. A similar reaction occurs between **1a** and adamantylphosphaalkyne; however, the product is highly soluble and difficult to isolate free from PPh_3 and, accordingly, was not studied further. The phosphaalkyne P≡$CC_6H_2(CMe_3)_3$-2,4,6 fails to react with **1a** under ambient conditions, presumably due to the enormous steric bulk of the aryl group. The complex **2a** appears to be indefinitely air-stable in the solid state and for hours in solution. Two possible orientations of hydrometalation are conceivable (Scheme 1) involving Ru−P (**A**) or Ru−C (**B**) bond formation, however, it is the former regiochemistry (**A**) which is realized in the ultimate product. The alternative orientation cannot be excluded as a possible but reversible kinetic detour; however, no evidence for its formation was obtained. Notably, Regitz has very recently observed the opposite regioselectivity of addition in the reactions of phosphaalkynes with tin hydrides.[11]

Despite repeated attempts to obtain structural data to confirm the nature of **2a**, severe positional disorder was encountered. The formulation therefore rests, albeit firmly, on spectroscopic data: FAB mass spectrometry reveals a substantial peak (53%) due to an adduct of the matrix 3-nitrobenzyl alcohol. The protonated molecular ion (10%) is accompanied by fragmentation due to loss of the phosphaalkenyl ligand (20%). The infrared spectrum (Nujol) is rather featureless, other than for a split absorption due to the carbonyl ligand (1929, 1918 cm^{-1}) and a weak absorption at 963 cm^{-1} which may arise in part from ν(PC). The $^{31}P\{^1H\}$ NMR spectrum of **2a** consists of a doublet resonance at 33.9 ppm due to the two equivalent phosphine ligands and a triplet to very low field at 450.4 ppm showing a coupling of ca. 10 Hz. This region of the ^{31}P NMR spectrum may be considered typical of phosphaalkenyl ligands;[8] however, this point will be returned to. In CD_2Cl_2 the vinylic proton gives rise to a double triplet resonance centered at δ 7.12 ppm showing coupling to both the phosphaalkenyl phosphorus [^2J(PC) = 16.8 Hz] and to the two chemically equivalent phosphine ^{31}P nuclei [$^4J(P_2H)$ = 2.3 Hz]. In C_6D_6 this resonance moves to 7.43 ppm and is more clearly distinguished from those due to the phosphine phenyl groups. The $^{13}C\{^1H\}$ NMR spectrum of **2a** includes a triplet resonance at 202.4 ppm [$J(P_2C)$ = 15.2 Hz] due to the carbonyl ligand and a set of virtual triplet resonances for the phosphine phenyl groups indicating a trans Ru(PPh_3)$_2$ arrangement, each

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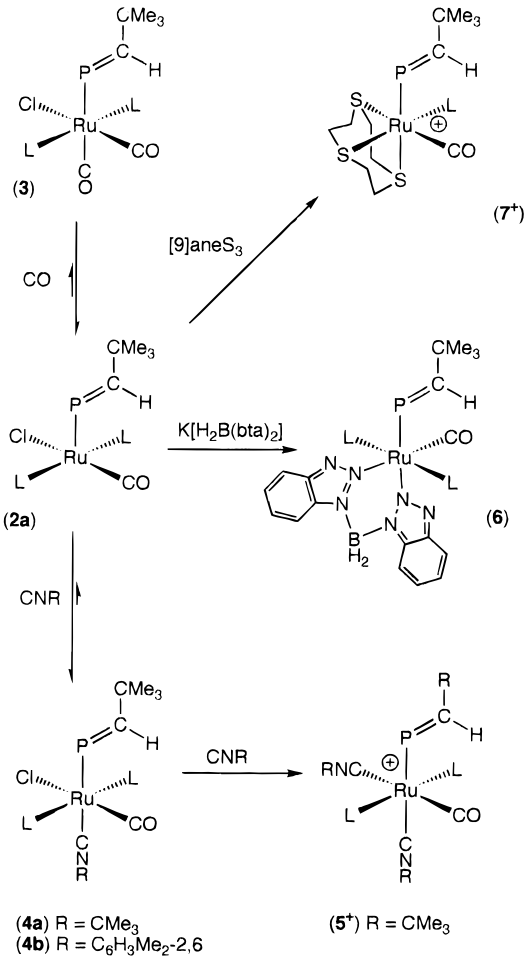
Scheme 2[a]

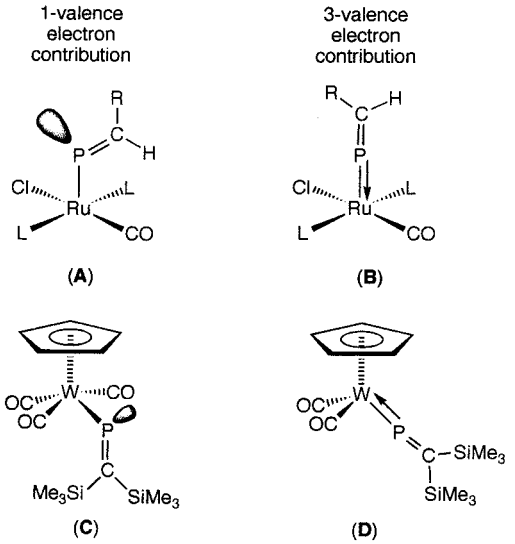


[a] L = PPh_3.

of these ligands being cis to the carbonyl ligand. A doublet resonance at 184.9 ppm [^1J(PC) = 58.9 Hz] is assigned to the phosphaalkenyl P=C carbon, while the CMe_3 group gives rise to two doublets at 40.8 [^2J(PC) = 10.7] and 30.8 ppm [^3J(PC) = 14.3 Hz].

Ligand Addition/Substitution Reactions (Scheme 2). The "$RuCl(CO)(PPh_3)_2$" fragment requires a further 3 valence electrons to complete its ideal effective atomic number (EAN). Phosphaalkenyl ligands have been observed to coordinate in two possible binding modes to mononuclear centers (Chart 1). The M−P−C spine can be nonlinear in which case there is a lone pair on phosphorus, and the ligand provides one valence electron in a simple σ-bond (**A**). Alternatively, the M−P−C spine may be linear in which case the ligand is considered to provide 3 valence electrons and might be referred to as a "phosphavinylidene". This dichotomy is best illustrated by the class of complexes [M{P=C($SiMe_3$)$_2$}$(CO)_x(\eta$-C_5R_5)] (M = Cr, Mo, W; R = H, Me; x = 3 (**C**), 2 (**D**)).[26−28] The complexes with a bent M−P−C spine may be thermally decarbonylated to dicarbonyl

Chart 1



complexes with linear M−P−C phosphavinylidene ligands. In some cases this reaction is spontaneous under ambient conditions and accompanied by a shift to *high field* of the position of the ^{31}P NMR resonance by 30−116 ppm. In the case of **2a** addition of carbon monoxide occurs rapidly but reversibly at room temperature. Thus the red color of **2a** is immediately discharged on addition of CO to provide pale yellow solutions of [Ru(P=CHCMe$_3$)Cl(CO)$_2$(PPh_3)$_2$] (**3**). If the complex is precipitated with hexane while under an atmosphere of CO, a pale yellow solid is isolated in 84% yield. The complex is however unstable in the absence of excess carbon monoxide (precluding satisfactory elemental microanalysis), reverting slowly to **2a** when stored as a solid or rapidly in solution. Thus while CO coordination is rapid, so is dissociation.

Infrared spectroscopy indicates a *cis*-dicarbonyl geometry [Nujol: ν(CO) = 2024, 1975 cm^{-1}], while the ^{31}P{^{1}H} NMR spectrum suggests a *trans*-bis(phosphine) arrangement indicated by the appearance of a doublet resonance at 22.1 ppm. However, most remarkable in this spectrum is the appearance of a broadened resonance at 369.5 ppm which is moved 81 ppm to *higher field* of that in **2a**. The direction of this change in chemical shift is opposite to those for the EAN-precise complexes **C** and **D**. While there is no question as to the coordination mode of the phosphaalkenyl ligand in 18-electron **3**, this counterintuitive spectroscopic result calls into question the nature of the bonding in **2a**. We suspect that the phosphaalkenyl ligand in **2a** does not involve a linear "phosphavinylidene" coordination but rather that the complex is coordinatively unsaturated with a bent and hence nucleophilic phosphaalkenyl ligand. Consistent with this interpretation, the complex **2a** has been found to react at phosphorus with a range of electrophiles, e.g., HCl, MeI, $ClAuPPh_3$, and $HgCl_2$.[9,29] The nature of the novel compounds obtained via electrophilic attack will be discussed in a subsequent paper.[30] These reactions however point toward a nucleophilic character for the phosphorus atom of the

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phosphaalkenyl ligand in **2a**, and thus, a nonlinear Ru−P−C spine might be reasonably inferred. It is quite possible that this is a general phenomenon for late transition metal phosphaalkenyl complexes with high d-occupancies (*cf. nitrosyls*), and we are currently attempting to broaden this currently narrow class of complex to explore this intriguing aspect.

As with the reaction of **2a** with CO to provide **3**, isocyanides also add to **2a**: Addition of 2,6-dimethyphenyl isocyanide to a dichloromethane solution of **2a** results in immediate decoloration to provide [Ru(P═CHCMe$_3$)Cl(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$] (**4b**). By analogy with the reactions of related 5-coordinate vinyl complexes[17,19] it may be assumed that coordination of the isocyanide occurs trans to the phosphaalkenyl ligand. The stereochemistry about the equatorial coordination plane does not however follow unambiguously from spectroscopic data. This has, however, been confirmed for the structurally characterized complex [RuCl(CO)(PHFCH$_2$CMe$_3$)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]$^+$ which results from the reaction of **4b** with excess HBF$_4$.[29] Once again addition of a two electron ligand to **2a** results in a shift of 59 ppm to high field for the triplet ^{31}P{^{1}H} NMR resonance due the phosphaalkenyl ligand (391.0 ppm). There is a marginal increase in the value of ^2J(P$_2$P) to 11.1 Hz upon coordinative saturation of ruthenium. The vinylic proton of the phosphaalkenyl ligand gives rise to a double triplet resonance at δ 8.12 ppm. The infrared spectrum of **4b** includes strong absorptions due to the isocyanide (2121, 2111sh cm^{-1}) and carbonyl (1962 cm^{-1}) ligands. The gross formulation is further supported by the appearance of a molecular ion in the FAB-mass spectrum in addition to fragmentations due to sequential loss of the phosphaalkenyl and chloride ligands. In contrast to the facile decarbonylation of **3**, solutions of **4b** only slowly dissociate the isocyanide to re-form **2a** [ca 5% over 2 days by IR spectroscopy].

A similar complex [Ru(P═CHCMe$_3$)Cl(CO)(CNCMe$_3$)(PPh$_3$)$_2$] (**4a**) is obtained on addition of CNCMe$_3$ to **2a** in dichloromethane; however, if excess isocyanide is added, the salt [Ru(P═CHCMe$_3$)(CO)(CNCMe$_3$)$_2$(PPh$_3$)$_2$]Cl **5**(Cl) is obtained via replacement of chloride by the more nucleophilic alkyl isonitrile. Samples of **4a** uncontaminated with **5**(Cl) are most conveniently obtained by carrying out the reaction in diethyl ether suspension, from which **4a** precipitates on formation, prior to reaction with excess CNCMe$_3$. Metathesis of the counteranion with Na[BPh$_4$] provides the salt **5**(BPh$_4$). Once again a nonlinear phosphaalkenyl ligand is required by EAN considerations, and this is manifest as a low-field resonance at 335.9 ppm in the ^{31}P NMR spectrum. In the solid state (Nujol) both the carbonyl and isocyanide infrared absorptions are split; however, in dichloromethane solution two isocyanide absorptions [ν(CN) 2179, 2156 cm^{-1}] and one carbonyl peak [ν(CO) 2021 cm^{-1}] are observed indicating that the two isocyanide ligands are mutually *cis*-coordinated. Thus the stereochemistry is confirmed to be that shown in Scheme 2.

The facile formation of **5**(Cl) points to a lability of the chloride ligand. Reactions with potentially polydentate ligands were therefore investigated briefly. As previously observed for the vinyl complexes [Ru(CH═CHR)Cl(CO)(PPh$_3$)$_2$],[21] **2a** reacts readily with K[H$_2$B(bta)$_2$] (bta = benzotriazolyl) to provide the neutral complex [Ru(P═CHCMe$_3$){H$_2$B(bta)$_2$}(CO)(PPh$_3$)$_2$] (**6**). Although the ^{1}H NMR spectrum of **6** includes a resonance at 0.81 due to the CMe$_3$ substituent and a very broad resonance at 3.95 due to the BH$_2$ group, the resonance due to the vinylic proton of the phosphaalkenyl ligand could not be unambiguously distinguished from the myriad of peaks arising from the phenyl and benzotriazolyl resonances. The ^{31}P{^{1}H} NMR spectrum comprised two peaks at 391.0 and 28.9 ppm corresponding to the phosphaalkenyl and phosphine phosphorus nuclei, respectively. The FAB-mass spectrum confirmed the formulation, with the appearance of a molecular ion in addition to fragmentations arising from loss of phosphine, H$_2$B(bta)$_2$, and P═CHCMe$_3$ groups.

The reaction of [Ru(CH═CHR)Cl(CO)(PPh$_3$)$_2$] with K[HB(pz)$_3$] (pz = pyrazol-1-yl) provides the complexes [Ru(CH═CHR)(CO)(PPh$_3$){HB(pz)$_3$}].[21] Similarly, **2a** reacts with K[HB(pz)$_3$] to provide [Ru(P═CHCMe$_3$)(CO)(PPh$_3$){HB(pz)$_3$}]. The formulation follows from spectroscopic data; however, it proved difficult to isolate this complex in analytically pure form. A more tractable and analogous complex was however obtained on treating **2a** with 1,4,7-trithiacyclononane ([9]aneS$_3$). Thus, by analogy with the synthesis of [Ru(CH═CHR)(CO)(PPh$_3$)([9]aneS$_3$)]Cl,[22] treating a dichloromethane solution of **2a** with [9]aneS$_3$ resulted in the formation of the salt [Ru(P═CHCMe$_3$)(CO)(PPh$_3$)([9]aneS$_3$)]Cl **7**(Cl) which could be converted to the more crystalline salt **7**(PF$_6$) on treatment with KPF$_6$. As in the previous examples, coordinative saturation at ruthenium is accompanied by a shift in the position of the phosphaalkenyl ^{31}P NMR resonance to higher field (357.3 ppm) and, together with the value for **5**(Cl), these two cationic complexes show the highest field resonances, relative to the neutral adducts obtained.

Thiocarbonyl Complexes (Scheme 3). The thiocarbonyl ligand CS,[31] while superficially analogous to CO, is a significantly more potent π-acid and is also more prone to migratory insertion processes.[32] We have previously shown that the hydrido−thiocarbonyl complex [RuHCl(CS)(PPh$_3$)$_3$] (**1b**)[13] reacts with alkynes via a hydrometalation sequence to provide σ-vinyl complexes analogous to those obtained with **1a**. The subsequent reaction of these complexes with [9]aneS$_3$ provides either the σ-vinyl complex [Ru{C(CO$_2$Me)═CHCO$_2$Me}(CS)(PPh$_3$)([9]aneS$_3$)]$^+$ or the thioacyl complexes [Ru(η^2-SCCR═CHR′)(PPh$_3$)([9]aneS$_3$)]$^+$ depending on the alkyne employed (Scheme 3).[22] A similar sequence was therefore investigated with P≡CCMe$_3$. Treating **1b** with P≡CCMe$_3$ provides high yields of the orange complex [Ru(P═CHCMe$_3$)Cl(CS)(PPh$_3$)$_2$] (**2b**). Spectroscopic data for **2b** are essentially comparable to those for **2a** with the exception of those associated with the thiocarbonyl ligand [ν(CS) = 1267 cm^{-1}(Nujol), δ(^{13}CS) = 297.7, ^2J(P$_2$C) = 15.2 Hz]. The complex **2b** reacts with both [Et$_2$NH$_2$][S$_2$CNEt$_2$] and [9]aneS$_3$ to provide the complex [Ru(P═CHCMe$_3$)(S$_2$CNEt$_2$)(CS)(PPh$_3$)$_2$] (**8**) and the salt [Ru(P═CHCMe$_3$)(CS)(PPh$_3$)-

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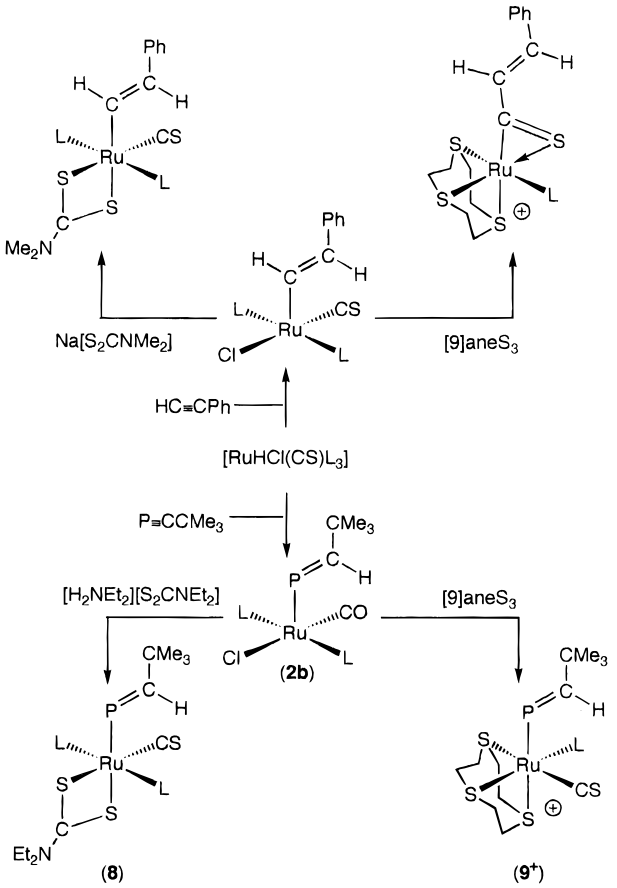
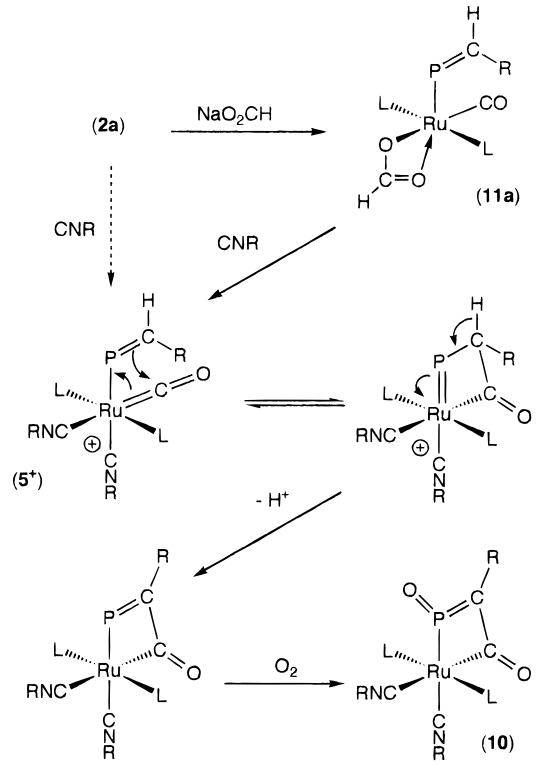
Scheme 3[a]



[a] L = PPh_3.

Scheme 4[a]



[a] L = PPh_3 and R = CMe_3.

([9]aneS$_3$)]Cl **9**(Cl**)**. The former result is not surprising, in that migratory insertion of thiocarbonyl and vinyl ligands does not occur when [Ru(CH═CHPh)Cl(CS)-(PPh_3)$_2$] is treated with Na[S_2CNMe_2], the product being [Ru(CH═CHPh)(S_2CNMe_2)(CS)(PPh_3)$_2$].[30] The latter result however is significant in that it suggests that the phosphaalkenyl ligand is less prone to migratory insertion processes than are simple vinyl ligands. The reactions of **2b** with carbon monoxide or isocyanides, by way of contrast, are complex and have yet to yield tractable products.

Formation of a λ^5-phosphaalkenyl Complex. While λ^3-phosphaalkenyl complexes are now well-known,[8] those based on formally pentavalent phosphorus (λ^5) have not been described. A λ^5-thiaphosphaalkenyl ligand has however been proposed as an intermediate to account for the products of addition of sulfur to the complex [W{P═C($SiMe_3$)$_2$}(CO)$_3$(η-C_5H_5)].[28] We have encountered an unusual metallacyclic example of a λ^5-oxaphosphaalkenyl ligand which results from the slow aerial decomposition of the complex **4a** in ethanol. The complex is formulated as [Ru{η^2-P(═O)C(CMe_3)C-(═O)}($CNCMe_3$)$_2$(PPh_3)$_2$] (**10**) on the basis of spectroscopic data and a single-crystal structure determination (Scheme 4).[10] Among the spectroscopic data for **10**, the phosphorus-31 chemical shift for the phosphaalkenyl group is perhaps the most remarkable in that it is shifted substantially to high field, appearing as a triplet at 47.0 ppm [$^2J(P_2P)$ = 25.2 Hz] ppm. In the intervening years since Roper's report of the first example of a metallacyclic phosphaalkenyl complex,[33] very few examples have since emerged and all involve two-coordinate λ^3-phosphorus.[34,35]

The complex **10** which contains two isocyanide ligands clearly results from a disproportionation involving loss of isocyanide from **4a** and coordination of this to a second molecule of **4a**. This is supported by the observation that **5**(Cl) is also decomposed slowly by air to provide **10**. The key step appears to involve nucleophilic attack by the β carbon of the phosphaalkenyl ligand upon the *cis*-carbonyl coligand. This is then presumably followed by deprotonation of the resulting metallacycle, the methine proton of which is α to both a carbonyl and a phosphino group, both of which would be expected to enhance the acidity. The reaction is slow (3−5 days), however, on addition of a nonnucleophilic base (DBU) to **5**(Cl) the reaction is accelerated and complete within 1 h. The proposed neutral metallacyclic intermediate has so far eluded isolation, being rapidly oxidized. Thus the proposed mechanism remains conjecture. The metallacyclic precursor to **10** might be viewed as an alternative coordination mode for the ketenylphosphinidene ligand which has been observed to result from phosphaalkyne/carbonyl coupling processes, albeit only in polynuclear systems.[36]

Carboxylate Complexes. The curious bonding proposed to occur for the complexes **2** remains speculative

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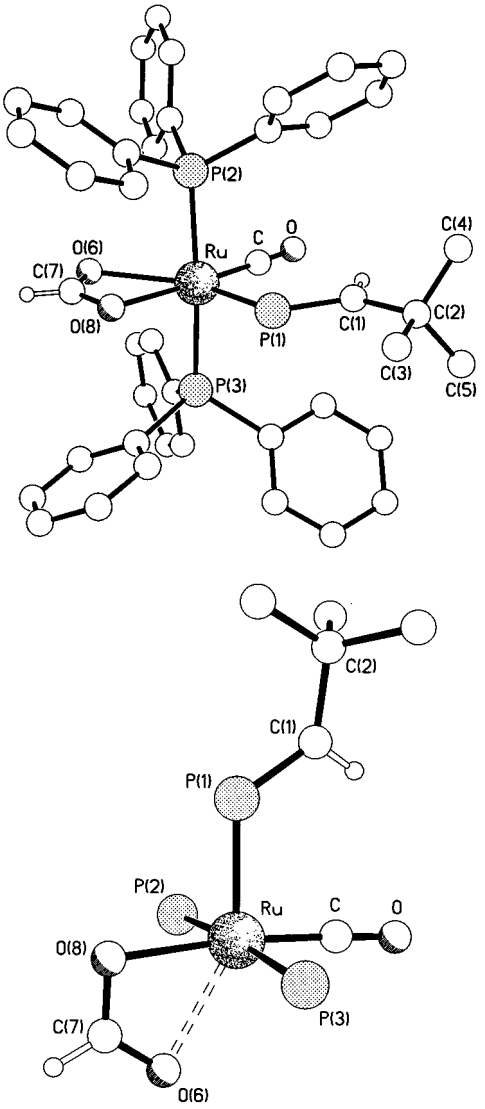

Figure 1. (a) Top: Molecular structure of the complex **11a**, showing 40% probability thermal ellipsoids, with methyl and phenyl H atoms omitted for clarity. (b) Bottom: View normal to equatorial coordination plane of **11a** with phosphine ligands omitted.

in the absence of accurate structural information. In an alternative approach to investigating this aspect, we reasoned that replacement of the chloride ligand by a weakly bidentate chelate might provide insight through differential trans influences for the phosphaalkenyl and carbonyl ligands. The reaction of **2a** with carboxylate salts was therefore investigated. A rapid reaction ensues between **2a** and the sodium salts of formic and ferrocenecarboxylic acids to provide the complexes $[Ru(P{=}CHCMe_3)(O_2CR)(CO)(PPh_3)_2]$ (R = H **(11a)**, $C_5H_4Fe(\eta\text{-}C_5H_5)$ **(11b)**). Spectroscopic data for these two derivatives (Experimental Section) are unremarkable alongside those for complexes **3**−**9**. The complex **11a** provided crystals suitable for X-ray analysis, the results of which are summarized in Tables 1 and 2 and Figure 1.

The geometry at ruthenium may be described as distorted octahedral with the primary distortion arising, as expected, from the small bite angle of the formate chelate [O(6)−Ru−O(8) 57.1(2)°]. The formate is, however, very asymmetrically bound to ruthenium such that the ruthenium−oxygen bond trans to the phosphaalkenyl ligand is very significantly longer (37σ) at 2.366(5) Å than that to O(8) [2.182(5) Å]. Excluding O(6), the geometry at ruthenium becomes only lightly distorted square-based pyramidal, with cis-ligand angles in the range 86.2(2)−94.5(2)°. The ruthenium atom is displaced by only 0.10 Å above the plane defined by P(2), P(3), C, and O(8), in the direction of P(1), thus further emphasizing the strong trans influence of the phosphaalkenyl ligand and the corresponding weak Ru−O(6) linkage. The formate ligand does not extend significantly beyond the steric shield of the "$Ru(PPh_3)_2$" double cone, precluding intermolecular interactions. Hence the asymmetry may be attributed exclusively to electronic effects at the ruthenium center.

The phosphaalkenyl ligand provides the primary focus of interest. Previous examples of structurally characterized "1-electron" phosphaalkenyl complexes[8] include $[Fe\{P{=}C(SiMe_3)_2\}(CO)_2(\eta\text{-}C_5Me_5)]$,[37] $[Fe\{P{=}C(NMe_2)_2\}(CO)_2(\eta\text{-}C_5Me_5)]$,[38] $[Fe\{P{=}C(SiMe_3)OSiMe_3\}(CO)_2(\eta\text{-}C_5H_5)]$,[39] and the recently reported complex $[Fe\{P{=}CHNPhN{=}C(NMe_2)_2\}(CO)_2(\eta\text{-}C_5Me_5)]$.[40] However, as noted in the Introduction, all these involve sterically cumbersome and/or π-interactive substituents which may be expected to influence the structural as well as the reactivity features. In these complexes the P=C mutliple bonds and the Fe−P=C angles fall in the ranges 1.680(9)−1.709(5) Å and 109.67(6)−126.2(3)°, respectively.

In the complex **11a** the trans regiochemistry is clearly evident at the P(1)−C(1) multiple bond, resulting from cis addition of the ruthenium hydride, thus confirming the regiochemistry proposed for **2** and derived complexes. The angle at P(1) is almost perfectly trigonal at 119.1(3)°. The P(1)−C(1) bond of 1.640(8) Å is clearly multiple; indeed, it is the shortest such separation to be observed for a 1-electron phosphaalkenyl ligand. The angle at C(1) is opened somewhat from the ideal sp^2-trigonal value [P(1)−C(1)−C(3) 127.4(7)]. The equatorial donor atoms of the coordination sphere and the atoms C(1), C(2), C(7), and O are essentially coplanar with the maximum deviation being only 0.06 Å by P(1). The Ru−P(1) separation of 2.295(2) Å is significantly shorter than the ruthenium phosphine distances of 2.378(2) and 2.386(2) Å (by ca. 44σ).

The phosphaalkene complexes $[Ru(MeP{=}CHCMe_3)ClI(CO)(PPh_3)_2]$,[41] $[Ru\{P(AuPPh_3){=}CHCMe_3\}Cl_2(CO)(PPh_3)_2]$,[42] and $[Ru\{P(HgC_5H_4Fe(\eta\text{-}C_5H_5)){=}CHCMe_3\}Cl_2(CO)(PPh_3)_2]$[43] have respectively Ru−P bond lengths of 2.280(2), 2.296(2), and 2.277(4) Å and P=C bond lengths of 1.657(8), 1.664(9), and 1.69(2) Å. These phosphaalkene complexes are derived from electrophilic attack at the phosphaalkenyl ligand of **2a**, and it is

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noteworthy that conversion of the phosphaalkenyl ligand into a coordinated phosphaalkene is not accompanied by crystallographically significant changes in the Ru−P or P−C bond lengths. Nevertheless, it has been argued that a π-acidic component to the bonding in the phosphaalkene complexes contributes to the short Ru−P bond lengths. It therefore seems likely that the Ru−P(1) bonding in **11a** also involves a modest π-component, consistent with the adopted orientation of this ligand such as to maximize π-retrodonation from ruthenium. That this feature is a result of the unsaturated P(1)═C(1) linkage follows from the observation that, in the conventional phosphido complex $[Os(PHPh)Cl(CO)_2(PPh_3)_2]$,[44] the osmium phosphido bond [2.523(7) Å] is significantly *longer* (15σ) than those involving the phosphine ligands [2.414(7), 2.423(6) Å].

Concluding Remarks. The hydrometalation of phosphaalkynes has been demonstrated for the first time. Following our preliminary communication,[9] the hydrostannylation of free phosphaalkynes has been reported.[11] Furthermore, the hydrozirconation of a platinum-coordinated phosphaalkyne has been recently observed by Nixon.[45] Taken together, these observation show that phosphaalkyne hydrometalation is a potentially useful method for the functionalization of phosphaalkynes. In the present case, the hydroruthenation process leads to versatile complexes of phosphaalkenyl ligands which do not require the presence of kinetically or thermodynamically stabilizing substituents at carbon. These serve as useful precursors to a wide range of phosphaalkenyl complexes. The reactivity and spectroscopic characteristics of the complexes **2** suggest a curious situation which appears to fall outside the previously dichotomous 1- or 3-electron-donating roles for such ligands. The inferred nonlinear nature of the Ru−P−C spine, not predicted by EAN considerations, renders the phosphorus nucleophilic, and the reactions of complexes **2** with electrophilic reagents will form the basis of a subsequent report.[30]

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Supporting Information Available: Tables of X-ray parameters, final atomic positional parameters and isotropic and anisotropic thermal parameters, and bond distances and angles and an ORTEP diagram for the structural analysis (8 pages). Ordering information given on any current masthead page.

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