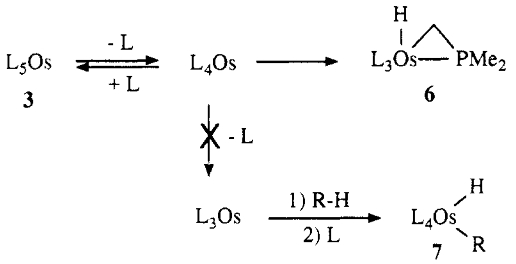
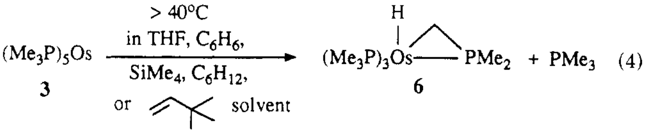
Scheme I



manipulation. Filtration of its solutions, even through carefully dried fritted disks results in formation of L_5OsH^+, identifiable by its characteristic ^{31}P NMR and its ^1H NMR hydride resonance (see below). We assume that the counterion is probably hydroxide, but we have not characterized this form of the salt. Centrifugation and decantation of solutions of **3** followed by careful solvent removal under vacuum yields solid ranging in color from off-white to orange, depending on the sample. Redissolution in various solvents often yields solutions of **3** which ^{31}P NMR shows to be clean and largely free of L. However, unless solvents and apparatus are scrupulously dried, substantial quantities of L_5OsH^+ are formed, even to the point of its being the only material present. Careful concentration of a pentane solution of **3** and cooling at −20 °C yielded a large, flat, nearly colorless crystal of **3** which displayed clean NMR spectra upon redissolution.[6]

Treatment of a THF solution of **3** at −78 °C with an ether solution of triflic acid yielded $[L_5OsH]OTf$, which has been fully characterized.[7] Thermolysis of **3** above 40 °C in neat THF, benzene, neohexene, tetramethylsilane, or alkane solvent results in quantitative formation of the Werner complex **6** (eq 4); no trace of product arising from attack on the solvent can be detected even in benzene or neohexene. (We know, for example, that $L_3Os(H)$(neopentyl) activates benzene,[5a,b] and L_3Os activates saturated C-H bonds intermolecularly.[5c,d]) In the presence of sufficient free L to keep [L] essentially constant, the conversion of **3** to **6** is cleanly first order, and the rate is strongly inhibited by the added L.



In the presence of a large excess of $P(CD_3)_3$, L′, the rate of ligand exchange with **3**, can be measured.[8] Preliminary rate data over the range of 30–50 °C yield an E_a of ca. 28 kcal/mol[8] for L dissociation. This rapid ligand exchange and the inhibition of reaction 4 by added L demonstrate that reaction 4 proceeds via presumably square-planar, phosphine-dissociated intermediate L_4Os, as in Scheme I. Intermediate L_4Os does not undergo dissociation of a second L to form L_3Os because we know that L_3Os would react with C_6H_6, $SiMe_4$, or neohexene with C–H activation to afford molecules of type **7**, none of which is observed.[5d]

Other reactions of **3** are under investigation.

Acknowledgment. We thank the National Science Foundation (CHE-8705228) for support of this work. Loans of heavy metal salts by Johnson Matthey Co. are gratefully acknowledged.

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(6) Elemental Anal. Calcd for $C_{15}H_{45}P_5Os$ (**3**): C, 31.58; H, 7.95. Found: C, 31.01; H, 8.26.

(7) Data for $L_5OsH^{+-}OTf$: ^1H NMR (THF-d_8) δ −12.22 (dp, 1 H, J_{PH} = 54.3, 21.7 Hz), 1.57 (d, 9 H, J_{PH} = 6.6 Hz), 1.75 (vt, 36 H, J_{PH}(apparent) = 5.3 Hz); $^{31}P\{^1H\}$ NMR (THF) δ −55.8 (d, 4 P, J_{PP} = 18.1 Hz), −60.9 (p, 1 P); ^{31}P\{selective ^1H, Os*H* coupled\} δ −55.8 (dd, J_{PH} = 18.0 Hz), −60.9 (dp, J_{PH} = 42.4 Hz); in this experiment, the ^1H decoupling band is centered at ca. δ + 5 ppm, and the hydride is slightly decoupled giving smaller hydride J_{PH} in the ^{31}P spectrum than in the ^1H spectrum. Anal. Calcd for $C_{16}H_{46}F_3O_3OsP_5S$: C, 26.63; H, 6.42. Found: C, 26.81; H, 6.56.

(8) The rate of exchange of L_5Os with L′ is monitored by ^1H NMR by following the disappearance of coordinated L at δ 1.5 and appearance of free L at δ 0.8. This rate is the composite of the rate for all five sequential displacements of L by L′ to form $(L')_5Os$. Assuming a negligible isotope effect on each subsequent displacement, k_{obsd} is 5 k_{dissoc}.

Synthesis and Reactivity of Ruthenium Hydride Complexes of Chelating Triphosphines. 2. X-ray Structure Determination of the Novel Compound Ru(CCPh)(η^3-PhC$_3$CHPh)(Cyttp) (Cyttp = $C_6H_5P(CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2)_2$)[1]

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Summary: The reaction of RuH_4(Cyttp) with phenylacetylene under mild conditions gives a unique type of compound Ru(CCPh)(η^3-PhC$_3$CHPh)(Cyttp) (**1**) which contains an acetylide and the unusual η^3-PhC$_3$CHPh carbon–carbon coupling product as ligands. Phosphorus-31, ^1H, and $^{13}C\{^1H\}$ NMR data in solution are consistent with the results of an X-ray single-crystal structure determination of **1**. This unusual complex contains the chelating triphosphine Cyttp in a meridional arrangement around ruthenium, a linear acetylide, and the η^3-PhC$_3$CHPh ligand, which is probably formed by end-to-end coupling of two phenylacetylene fragments.

During a study of the reactivity of acetylenes with RuH_4(Cyttp),[3] we found that a carbon–carbon bond formation reaction of phenylacetylene occurred under mild conditions. The isolated ruthenium complex Ru(CCPh)(η^3-PhC$_3$CHPh)(Cyttp) contains a linear acetylide and a novel η^3-PhC$_3$CHPh ligand, which might be considered as an intermediate in catalytic oligomerization or polymerization reactions of terminal acetylenes. We report herein the synthesis and structure of this unusual compound.

Treatment of RuH_4(Cyttp) with excess phenylacetylene in benzene at room temperature resulted in formation of Ru(CCPh)(η^3-PhC$_3$CHPh)(Cyttp) (eq 1).[4] The product is a red solid, which was isolated in 86% yield, based on

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[‡] Deceased December 7, 1988.

(1) Presented at the 3rd Chemical Congress of North American, Toronto, June 1988; abstract INOR 600. For part 1, see ref 3.

(2) (a) The Ohio State University. (b) University of Delaware.

(3) Jia, G.; Meek, D. W. *J. Am. Chem. Soc.* **1989**, *111*, 000.

(4) A mixture of 0.3 mL of phenylacetylene and RuH_4(Cyttp) (ca. 0.40 mmol, prepared from the reaction of 0.30 g of $RuCl_2$(Cyttp) with excess NaH) in 30 mL of benzene was stirred at room temperature for 3 h to give a deep red solution. The reaction mixture was then pumped to dryness. The residue was washed with 10 mL of MeOH to give a red powder. The powder was then collected on a filter frit, washed with MeOH, and dried under vacuum overnight; yield 0.34 g, 86% based on $RuCl_2$(Cyttp). X-ray quality crystals were obtained by slowly evaporating solvents from a saturated solution in CH_2Cl_2/MeOH with a stream of argon. Elemental Anal. Calcd: C, 72.63; H, 7.82. Found: C, 72.57; H, 7.83.

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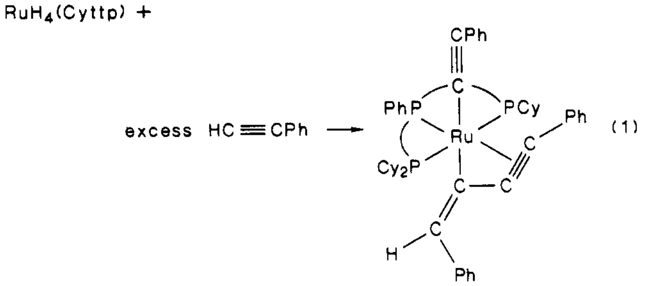


(1)

ruthenium. It was recrystallized from CH_2Cl_2/MeOH to give red crystals suitable for X-ray diffraction studies. Its ^1H NMR spectrum in CD_2Cl_2 displayed a resonance at δ 6.8, which is assigned to the vinyl proton, in addition to the normal resonances due to phenyl (δ 7.0–8.4) and cyclohexyl and methylene groups (δ 0.6–3.0) of the triphosphine ligand. The carbon–carbon triple bond stretching frequency of the acetylide ligand was observed at 2060 cm^{-1}. Both the ^{31}P NMR and the ^{13}C NMR data indicate that the triphosphine ligand is meridional around ruthenium.[5] On the basis of the spectroscopic data, we were unable to propose a definitive structure for this compound.

A single-crystal X-ray diffraction study was undertaken to define the structure of Ru(CCPh)(η^3-PhC_3CHPh)-(Cyttp);[6] the results are shown in Figure 1. The overall geometry around ruthenium is roughly octahedral. The three phosphorus atoms are bound to ruthenium in a meridional fashion as seen in solution by its $^{31}P\{^1H\}$ NMR spectrum. The phenylacetylide group is nearly linear and is cis to the three phosphorus atoms of the triphosphine. The distances between ruthenium and C(7) and between C(7) and C(8) are 2.037 (3) and 1.205 (5) Å, respectively, which are consistent with the distances observed for other ruthenium acetylide complexes.[7]

The most surprising feature of the compound is the presence of a η^3-PhC_3CHPh ligand, which must have been formed by end-to-end coupling of two phenylacetylene fragments. The distances between ruthenium and C(9), C(53), and C(54) are comparable at 2.200 (3), 2.191 (3), and 2.258 (3) Å, respectively. The bond length between C(9) and C(53) is 1.379 (5) Å, which is very similar to C–C bond distances in η^3-allyl complexes.[8] The bond distance between C(53) and C(54) is 1.249 (5) Å, which is in the range of carbon–carbon triple bond lengths in π-acetylene complexes (generally observed to range from 1.22 to 1.32 Å).[9] The angles C(10)–C(9)–C(53), C(9)–C(53)–C(54), and C-(53)–C(54)–C(60) suggest hybridization intermediate between sp and sp^2 for the central carbons, C(9), C(53), and C(54), of the C_4 connection between the phenyl groups.

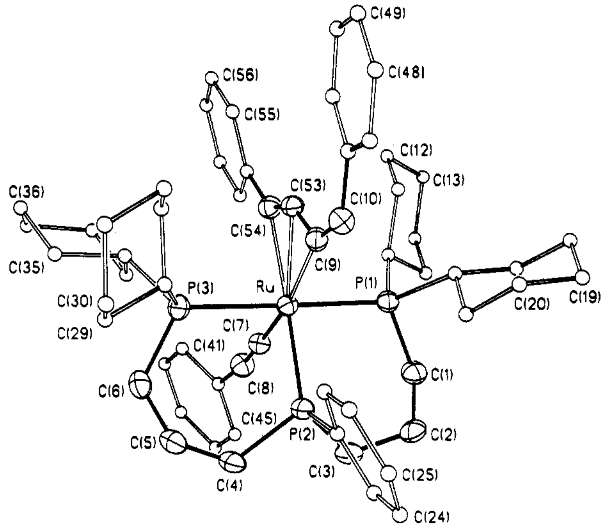
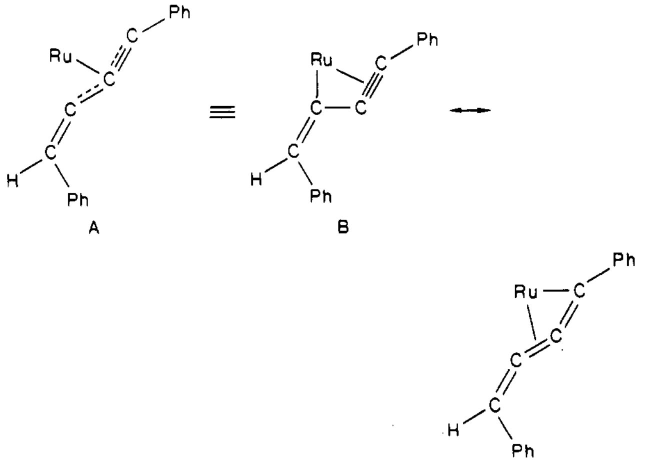


Figure 1. Molecular structure of Ru(CCPh)(η^3-PhC_3CHPh)-(Cyttp). The cyclohexyl and phenyl rings are drawn with arbitrary size spheres to enhance clarity. Bond distances (Å) and angles (deg): Ru–P(1), 2.405 (1); Ru–P(2), 2.290 (1); Ru–P(3), 2.417 (1); Ru–C(7); 2.037 (3); Ru–C(9), 2.200 (3); Ru–C(53), 2.191 (3); Ru–C(54), 2.258 (3); C(9)–C(10), 1.339 (5); C(9)–C(53), 1.379 (5); C(53)–C(54), 1.249 (5); C(7)–C(8), 1.205 (5); P(1)–Ru–P(2), 90.6 (1); P(1)–Ru–P(3), 176.2 (1); P(2)–Ru–P(3), 91.5 (1); P(1)–Ru–C(7), 88.0 (1); P(2)–Ru–C(7), 82.4 (1); P(3)–Ru–C(7), 89.2 (1); P(1)–Ru–C(9), 90.9 (1); P(2)–Ru–C(9), 110.9 (1); P(3)–Ru–C(9), 91.3 (1); C(7)–Ru–C(9), 166.7 (1); P(1)–Ru–M, 91.5 (2) (M = midpoint of C(53)–C(54)); P(2)–Ru–M, 163.9; P(3)–Ru–M, 87.4 (2); C-(7)–Ru–M, 113.6 (3); C(9)–Ru–M, 53.1 (3); Ru–C(7)–C(8), 178.1 (3); Ru–C(9)–C(10), 155.6 (3); C(10)–C(9)–C(5), 133.0 (3); C-(9)–C(53)–C(54), 148.7 (3)°.

On the basis of the X-ray diffraction results, the Ru-(η^3-PhC_3CHPh) fragment can be best described as form A, which is a combination of resonance forms B and C. To our knowledge this η^3-C_3 type of complex is still very rare in the literature, although η^3-allyl complexes are abundant.[10] The only precedent that we have found is the



A

B

C

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[5] Its ^{31}P NMR spectrum in CD_2Cl_2 exhibited a doublet for the two terminal phosphorus atoms at δ 2.5 and a triplet for the central phosphorus atom at δ 19.6 (J_{PP} = 37 Hz); thus, the chelating triphosphine occupies a meridional arrangement in the coordination sphere. In its ^{13}C NMR spectrum, resonances ranged from δ 118 to δ 158 in the aromatic region and from δ 17.3 to δ 37.7 in the aliphatic region. Virtual triplets at δ 37.7 (t, J = 7.5 Hz) and 35.7 (t, J = 8.4 Hz) were observed for the ipso carbon atoms of the cyclohexyl groups on the terminal phosphorus atoms, which confirm that the two terminal phosphorus atoms of Cyttp are trans to each other.

[6] Crystal data: $C_{60}H_{77}P_3Ru$, triclinic, $P\bar{1}$: a = 11.566 (3), b = 12.532 (3), c = 19.328 (7) Å; α = 90.49 (3), β = 102.42 (3), γ = 108.03 (3)°; V = 2593 (1) $Å^3$; Z = 2; D(calcd) = 1.226 g cm^{-3}; μ(Mo Kα) = 4.2 cm^{-1}; T = 293 K. Of 8414 data collected (Nicolet R3m/μ diffractometer, 4° ≤ 2θ ≤ 48°) and absorption corrected, 8142 were independent and 6540 were observed ($\geq 5\sigma(F_o)$). The Ru atom was located by heavy-atom methods. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were idealized (except for H(10) which was found and isotopically refined). The four phenyl rings were constrained to rigid hexagons: R_F = 3.76%, R_{wF} = 4.29%, GOF = 1.266, $\Delta(\rho)$ = 0.63 e $Å^{-3}$, and N_o/N_v = 12.3. SHELXTL (5.1) software was used for all computations (Nicolet XRD, Madison, WI).

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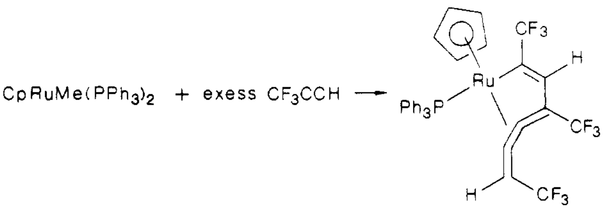
compound $[Os(\eta^3\text{-}PhC_3CHPh)(PMe_3)_4]PF_6$, which was obtained by oxidation of *cis*-$Os(C_2Ph)_2(PMe_3)_4$ with $AgPF_6$.[11] However, in this osmium complex, the Os–C bonding distances (2.39 (1), 2.21 (1), and 2.15 (1) Å) are not comparable, in contrast to the comparable Ru–C distances observed for our compound.

Interestingly, reactions between phenylacetylene and $MH(O_2CCF_3)(CO)(PPh_3)_2$ (M = Ru, Os) also give $M(PhC_3CHPh)(O_2CCF_3)(CO)(PPh_3)_2$; however, in these two compounds, the C–C triple bond is not bound to the metal.[12] The compound $Os(PhC_3CHPh)(O_2CCF_3)(PPh_3)_2$ is an active oligomerization catalyst for phenylacetylene; thus, it has been suggested as an intermediate in the catalytic oligomerization of phenylacetylene by $OsH(O_2CCF_3)(CO)(PPh_3)_2$.[12] The reaction of CF_3CCH with $CpRuMe(PPh_3)_2$ also gives a C–C coupling product (eq 2).[13]



(2)

The product could be viewed as a coupling reaction between CF_3CCH and an intermediate like we found (e.g., $Ru(\eta^3\text{-}CF_3C_3CHCF_3)$), although the authors[13] proposed an alternative mechanism for its formation. Thus, our $Ru(CCPh)(\eta^3\text{-}PhC_3CHPh)(Cyttp)$ complex could be regarded as an intermediate in catalytic polymerization or oligomerization reactions of terminal acetylenes. Formation of compound **1** could occur either by oxidative coupling of phenylacetylene, via the complex $RuH_4(Cyttp)$, or by insertion of a phenylacetylene fragment into a Ru–acetylide bond. The insertion reaction probably involves an intermediate such as $Ru(PhC{\equiv}CH)(C{\equiv}CPh)_2(Cyttp)$, which rearranges into $Ru(C{=}CHPh)(C{\equiv}CPh)_2(Cyttp)$,[14] followed by coupling of the vinylidine group and one of the acetylide ligands.[15] Since we have characterized $RuH_4(Cyttp)$ as the η^2-H_2 complex $RuH_2(H_2)(Cyttp)$,[3] we prefer the insertion process. Additional experiments are being conducted to define the mechanism of formation of the C_4 connecting chain.

Acknowledgment. We are grateful to the Johnson Matthey Co. for a loan of "$RuCl_3{\cdot}3H_2O$". We thank Professor Andrew Wojcicki for help in the preparation of the manuscript.

Registry No. 1, 119997-07-8; $RuH_4(Cyttp)$, 118575-30-7; $HC{\equiv}CPh$, 536-74-3.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates (8 pages); a listing of observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

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[14] See, for example: Birdwhistell, K. R., Tonker, T. L., Templeton, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 1401 and references on p 1405.

[15] Such a step has been proposed for the formation of $[Os(\eta^3\text{-}PhC_3CHPh)(PMe_3)_4]PF_6$ by treatment of $Os(C{\equiv}CPh)_2(PMe_3)_4$ with $AgPF_6$.

Book Reviews

Solvents and Solvent Effects in Organic Chemistry. By Christian Reichardt. VCH, Weinheim. 1988. xxii + 534 pp. $98.00

The title of this book is unnecessarily restrictive. Although examples are drawn almost exclusively from organic chemistry, the contents should be useful to almost any chemist concerned with solvent effects on reaction rates, equilibria, or physical properties. One chapter describes various interactions between solutes and solvents. Another surveys classifications of solvents based on chemical constitution, physical constants, acid–base behavior, specific solute–solvent interactions, or multivariate statistical methods. A chapter reviews solvent effects observed on acid–base, tautomeric, conformational, cis–trans, valence isomerization, and electron-transfer equilibria. A lengthy chapter reviews solvent effects observed on the rates and product compositions of a wide variety of reactions. Another chapter reviews solvent effects on UV–visible, fluorescence, ORD and CD, infrared, ESR, and NMR spectra. The final chapter describes various empirical parameters that have been developed to characterize solvents. A useful appendix has 10 tables that contain considerable practical information about preparation, purification, and various uses of solvents.

Those familiar with the first edition will find this second edition updated and greatly enlarged. As just one example, the new edition includes many more comparisons of behavior in solution with that in the gas phase. The number of references has doubled to nearly 2500; some early 1987 references are included.

Each reader probably will find, as I did, some detail of the presentation to quibble with, an area that is reviewed less critically than others, and a topic that is slighted. Such minor disagreements, however, are almost inevitable with a book so ambitious and broad in its coverage. This is an immensely useful book, and the source that I would turn to first when seeking virtually any information about solvent effects. Any graduate student should benefit from reading it. Every chemistry library should have a copy, and probably many chemists will want a personal copy. The publishers might consider issuing a paperbound edition with a price that would encourage individual ownership.

Herman G. Richey, Jr., *The Pennsylvania State University*