microsolutions result in the evoluton of a single species absorbing strongly at 400 and 790 nm (Figure 4A). (These data should be contrasted with those for Zr/toluene/Ar 12-K matrix cocondensations, which show a major absorption at 360 nm and which is believed to be associated with the authentic $(\eta^6\text{-}C_6H_5CH_3)_2Zr$[26] complex). In situ addition of PEt_3 to this solution at 140 K causes a rapid spectral transformation (Figure 4D) with new bands at 350 and 432 nm believed to be characteristic of $(\eta^6\text{-}C_6H_5CH_3)_2Zr(PEt_3)$. The remarkable reactivity of these Zr/toluene/MCH 140-K solutions can be appreciated from the spectral alterations induced by in situ addition of CO(383, 612 nm), N_2(400, 610 nm) (see for example, Figure 4C,B) and THF (410, 840 nm). The resemblance of these optical data to that of the product of depositing Zr vapor with DC510 at 250 K, 375, 470 nm (Figure 4E) is noteworthy. Of interest also is the observation that the species formed on reacting Zr/toluene/MCH 140-K solutions with THF will not react further with CO but is converted by PEt_3 to the postulated $(\eta^6\text{-}C_6H_5CH_3)_2Zr(PEt_3)$ complex, as evidenced by the growth of bands at 350 and 432 nm (vide supra). The Zr/toluene microsolution optical data and ligand displacement information can be tentatively rationalized in terms of a 16-electron bis(toluene)zirconium(0) complex, in which the vacant coordination site may be occupied by a weakly bonding, possibly η^2-toluene, ligand. Work is also continuing on this fascinating system.

The aforementioned examples rather convincingly demonstrate the feasibility of spectroscopically probing the progress of metal vapor-solution reactions and subsequent in situ ligand additions by using optical spectroscopy. An extension to other forms of spectroscopy is straightforward. Clearly the method holds great potential for studying the spectroscopy and chemistry of organometallic reactive intermediates in solution and for optimizing the yields and elucidating the thermal stabilities of specific products in macroscale metal vapor-solution syntheses.

Acknowledgment. The generous financial assistance of the Natural Sciences and Engineering Research Council of Canada's Operating and Strategic Energy Programmes is greatly appreciated. L.N. and M.A. also acknowledge the NSERC and the Ontario Provincial Government for graduate scholarships.

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$Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)$: A Square-Pyramidal Ruthenium Cluster with a Single μ_4-Bound Acetylide

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The potential utility of polynuclear transition-metal clusters in homogeneous catalysis has spurred efforts to investigate the chemistry of unsaturated molecules bound in multisite fashion to several metal atoms.[1] In the specific context of CO hydrogenation it has been suggested that $\mu_2\text{-}\eta^2$ or $\mu_3\text{-}\eta^2$ bonding of CO may be important in CO activation, particularly to C-O bond cleavage, generating carbidic carbon atoms.[2] Although there is recent evidence that cluster-bound carbides show unique reactivity,[3,4] knowledge of the chemical behavior of cluster carbides, or their relatives the cluster-bound acetylides, is generally lacking.

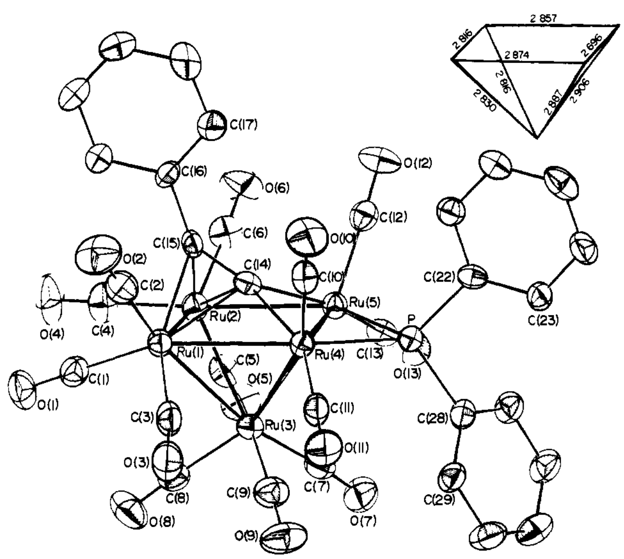

Figure 1. Polyhedral stereochemistry of $Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)$. Skeletal Ru-Ru bond lengths are shown (inset). Other important bond lengths and angles not mentioned in the text are Ru(4)-P 2.294 (2), Ru(5)-P 2.278 (2) Å; ∠Ru(4)-C(14)-Ru(5) 79.7 (0), ∠Ru(1)-C(14)-Ru(2) 79.1 (0), ∠C(14)-C(15)-Ph 141.4 (4)°.

In exploring the patterns of reactivity for sideways-bound acetylides, we have synthesised and characterized a unique square-pyramidal ruthenium carbonyl cluster in which the acetylide is bonded in a hithertofore unknown $\mu_4\text{-}\eta^2$ fashion. No pentanuclear carbonyl clusters of ruthenium have yet been structurally characterized, and, indeed, this stereochemistry is relatively rare for other metals.[5,6] Within the iron subgroup only $Fe_5(CO)_{15}C$,[7] $Fe_5N(CO)_{14}H$,[8] and $Os_5(CO)_{15}(POMe)$,[9] all with square-pyramidal metal skeletons, have been structurally characterized.[10] The molecule $Ru_5(CO)_{13}$ $(C{\equiv}CPh)(PPh_2)$ is a member of the interesting acetylide series $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C_2R)(PPh_2)$, $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2R)(PPh_2)$, $Ru_3(CO)_6(\mu_2\text{-}CO)_2\text{-}(\mu_3\text{-}\eta^2\text{-}C_2R)(PPh_2)$ (R = Ph, *i*-Pr, *t*-Bu), and $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C_2R)(PPh_2)(R{=}Ph)$.[11]

The pentanuclear cluster is generated thermally. Heating the monosubstituted ruthenium cluster $Ru_3(CO)_{11}(PPh_2C{\equiv}CPh)$ in heptane at 70 °C for 8 h results in fragmentation of the starting material to give predominantly the dinuclear carbonyl acetylide $Ru_2(CO)_6(C{\equiv}CPh)(PPh_2)$,[11] a hexanuclear product, as yet uncharacterized, and $Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)$ which precipitates from the reaction mixture in 30% yield on concentration in vacuo.[12] Infrared studies[13] confirmed the presence of only terminal carbonyl groups and a ^{31}P NMR spectrum suggested a single phosphido

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(12) The pentanuclear cluster was separated from traces of $Ru_3(CO)_{12}$ by dissolution in benzene, followed by chromatography through a short (12 cm) Florisil column. Blue-black crystals were obtained from heptane-benzene solutions (yield 30%), mp 214-216 °C. Anal. Calcd: C, 34.29; H, 1.31; P, 2.68. Found: C, 34.62; H, 1.35; P. 2.68.

(13) IR ν(CO) (C_6H_{12}) 2076 m, 2043 vs, 2024 s, 2014 m, 2000 w cm^{-1}; ^{31}P NMR (C_6D_6) δ (with respect to 85% H_3PO_4) +253.

bridge between two strongly bonded ruthenium atoms.[11,13]

The structure was determined by a single-crystal X-ray diffraction study.[14] An ORTEP II plot is illustrated in Figure 1, which also provides bond length data (inset) for the metal framework. The five ruthenium atoms form a square-based pyramid with Ru(1), Ru(2), Ru(4), and Ru(5) defining the base and Ru(3), the apex. Apical Ru(3) lies 2.086 Å above the best plane[15] defined by the four basal metal atoms and is slightly displaced away from the basal edge [Ru(4)–Ru(5)] bridged by the phosphido group. The base of the pyramid is slightly but significantly distorted toward a rectangle with the shorter Ru–Ru bond [Ru(4)–Ru(5) = 2.696 (1) Å] bridged by a phosphido group occupying equatorial sites. The remaining seven Ru–Ru distances (average, 2.855 Å) are normal, as compared to bond lengths in other ruthenium clusters,[16] with no single bond length deviating by more than 0.04 Å from the mean. The lack of structural data for any other square-pyramidal Ru_5 cluster precludes a more detailed analysis. The acetylide which bridges the Ru(4)–Ru(5) edge in symmetrical fashion is simultaneously η bonded to the remaining two basal atoms Ru(1) and Ru(2). The Ru(4)–C(14) [2.114 (8) Å] and Ru(5)–C(14) [2.095 (8) Å] distances are significantly shorter than the corresponding Ru–C (acetylide) distances [Ru(2)–C(19) 2.22(1) and Ru(3)–C(19) 2.185(9) Å] in $Ru_3(CO)_6$ $(\mu_2\text{-}C{\equiv}Bu\text{-}t)_2(PPh_2)_2(Ph_2PC_2Bu\text{-}t)$[11] where, however, the symmetrically bridging acetylide is not involved in η bonding with other metal atoms. Comparison of ruthenium–carbon (acetylide) bond lengths in $Ru_5(CO)_{13}(\mu_4\text{-}C_2Ph)(PPh_2)$ [Ru(1)–C(14) 2.190 (8), Ru(1)–C(15) 2.216 (8), Ru(2)–C(14) 2.234(8), Ru(2)–C(15) 2.163(9) Å] with corresponding values in $Ru_3(CO)_9(\mu_3\text{-}C_2Pr\text{-}i)(PPh_2)$ [average Ru–C (acetylide) 2.321 Å] and $Ru_2(CO)_6$$(\mu_2\text{-}C_2Bu\text{-}t)(PPh_2)$[11] [average Ru–C (acetylide) 2.350 Å] indicates a significant increase in the strength of metal–acetylide bonding as the number of interacting metal atoms increases. As a result of the strong η interactions with Ru(1) and Ru(2), the carbon–carbon triple bond is lengthened to 1.342 (11) Å. This distance which is characteristic of uncoordinated alkene double bonds is the greatest we have yet observed for σ-η-acetylide complexes of group 8 metals.

Remarkably, the stereochemistry of the acetylenic carbon atom C(14) is planar[18] in contrast to the marked cis or trans bending at both carbon atoms which usually accompanies μ_2- or μ_3-alkyne or acetylide bonding. Figure 1 also illustrates that C(14) occupies a capping site on the Ru(1)–Ru(2)–Ru(4)–Ru(5) face, with the five ruthenium atoms and C(14) defining a distorted octahedron. This stereochemistry is reminiscent of the cluster carbide $Fe_5(CO)_{15}C$,[7] although in the present case the capping atom remains part of an acetylide. Athough a stereochemical similarity between $Fe_5(CO)_{13}C$ and $Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)$ is evident, further speculation on a possible conversion of the latter to a cluster carbide and on the chemical behavior of the multisite-bound acetylide must await the results of experiments currently in progress.

Finally, in view of current interest in ^{31}P (PPh_2) chemical shift correlations with M–M bond lengths, we note that the very low field ^{31}P chemical shift of the PPh_2 group in $Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)$ is consistent with the presence of a very strong Ru–Ru bond [Ru(4)–Ru(5) = 2.696 (1) Å] and short Ru–P bond lengths (average 2.286 Å) rather than an unusually small Ru(4)–P–Ru(5) angle.[19]

Acknowledgment. We are grateful to NSERC and Imperial Oil for financial support of this work.

Supplementary Material Available: Fractional atomic coordinates (Table S1), hydrogen atom coordinates and isotropic thermal parameters (Table S2), and anisotropic thermal parameters (Table S3) for $Ru_5(CO)_{13}(C_2Ph)(PPh_2)$ (3 pages). Ordering information is given on any current masthead page.

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(14) Dark blue crystals of $Ru_5(CO)_{13}(C_2Ph)(PPh_2)$ are monoclinic, space group $P2_1/n$ with $a = 9.966$ (2), $b = 16.877$ (2), $c = 21.707$ (4) Å; $\beta = 100.51$ (2)°; $Z = 4$; $\rho_m = 2.14$, $\rho_c = 2.139$ g cm^{-3}; $\mu_{MoK\alpha} = 21.15$ cm^{-1}; $F(000) = 2208$. The structure was solved and refined by using 3335 observed [$I \geq 3\sigma(I)$], independent reflections measured on a Syntex $P2_1$ automatic diffractometer using Mo Kα radiation out to $2\theta \leq 45°$. With all nonhydrogen atoms having anisotropic thermal parameters and hydrogen atoms isotropic coefficients, the structure was refined by full-matrix least-squares methods to R and R_w values of 0.033 and 0.039, respectively.

(15) The atoms Ru(1), Ru(2), Ru(4), and Ru(5) deviated by less than ±0.02 Å from the mean plane through these atoms.

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(18) The atom C(14) deviates by only 0.060 Å from a least-squares plane containing Ru(4), Ru(5), and C(15).

(19) The Ru(4)–P–Ru(5) angle of 72.30 (0)° does not differ markedly from the Ru–P–Ru angle [72.0 (0)° in $Ru_2(CO)_6(C{\equiv}CBu\text{-}t)(PPh_2)$ [δ (^{31}P) +123.9] but the Ru–Ru bond length, 2.752 (1) Å, and Ru–P distances (average, 2.339 Å) in the latter are significantly longer.

Large, Inverse Solvent Isotope Effects: A Simple Test for the E1cB Mechanism[1]

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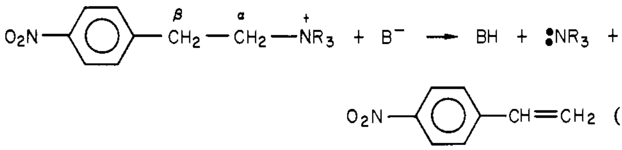
We wish to report a large, inverse solvent deuterium isotope effect on the initial rates of base-induced *p*-nitrostyrene formation from [β-(*p*-nitrophenyl)ethyl]ammonium ions in aqueous acetohydroxamate buffers (eq 1). For compounds **1a** and **1b**, the magnitude of the inverse effect can be increased by increasing the buffer concentration (at constant buffer ratio). This variation is quantitatively accounted for by application of the steady-state approximation to the ElcB mechanism (eq 2) and serves as a sensitive test for that mechanism *whenever the proton-transfer step is not entirely rate controlling.*



(1)

1a, :NR_3 = trimethylamine ($pK_a = 9.85$)
b, :NR_3 = quinuclidine ($pK_a = 11.45$)
c, :NR_3 = 4-methyl-1,4-diazabicyclo[2.2.2]octanium ($pK_a = 3.01$)[2]

$$>C{-}H \underset{k_{-1}[BH]}{\overset{k_1[B^-]}{\rightleftharpoons}} >C^- \xrightarrow{k_2} \text{products} \qquad (2)$$

In the figure are shown plots of experimental first-order rate constants for reaction of compound **1b** in H_2O and D_2O, both against acetohydroxamate concentration. Three features are of interest: (1) The plots are curved. For the reaction in H_2O, buffer saturation is observed indicating a complete change of rate control from step 1 (proton transfer) to step 2 (leaving group departure). The buffer curvature for both solvents is quantitatively described by the steady-state analysis of the E1cB mechanism (see below) from which the lines through the experimental points were calculated. Similar, but less marked, curvature has been observed previously with increasing concentrations of substituted-quinuclidine buffers in H_2O.[2] (2) The observed rate constants are larger in D_2O than in H_2O. (3) The inverse solvent isotope effect

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