CO-Induced $C(sp^2)/C(sp)$ Coupling on Ru and Os: A Comparative Study

Dejian Huang, Montserrat Oliván, John C. Huffman, Odile Eisenstein,*,† and Kenneth G. Caulton*,‡

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405-4001, and LSDSMS (UMR 5636) Case Courrier 14, Université de Montpellier 2, 34095 Montpellier Cedex 5, France

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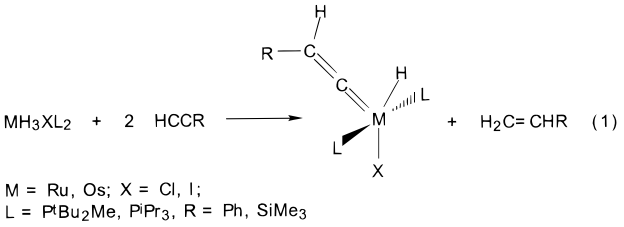
Reaction of $OsHCl({=}C{=}CHSiMe_3)(P^iPr_3)_2$ with $HC{\equiv}CSiMe_3$ gives $OsCl\{(E)\text{-}CH{=}CHSiMe_3\}(C{=}CHSiMe_3)(P^iPr_3)_2$, which reacts with excess CO to give the C−C coupling product $OsCl\{C(CH{=}CHSiMe_3){=}CHSiMe_3\}(CO)_2(P^iPr_3)_2$. Reaction of $[RuH(CO)(P^tBu_2Me)_2]^+$ (as its $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$ salt) with 2 mol of $HC{\equiv}CSiMe_3$ gives immediately the C−C coupling product $[Ru\{\eta^3\text{-}(Me_3Si)CH{=}C{-}CH{=}CH(SiMe_3)\}(CO)(P^tBu_2Me)_2]^+$. The crystal structure of this latter product reveals one agostic ^tBu C−H interaction with Ru. Ab initio (DFT B3LYP) calculations show the presence of two isomeric structures as minima on the potential energy surface, one with vinyl and vinylidene ligands, and the other with a butadienyl ligand bonded in an η^3 manner to the metal. The calculations show a strong preference for the butadienyl structure when the metal fragment is $Ru(CO)L_2^+$ and a nearly degenerate situation when the metal fragment is $OsClL_2$ ($L = PH_3$).

Introduction

This is a study of two initially distinct research themes which converge and which, taken together, reveal more than either individual result.

The molecules MH_3ClL_2 ($M = Ru$, Os and $L = P^iPr_3$ or P^tBu_2Me) are dehydrogenated by terminal alkynes according to eq 1. One molecule of alkyne is rearranged



(hydrogen migration), and the result is a 16-electron (carbonyl-free) vinylidene complex.[1] The remaining M−H moiety is a potential site for addition of added alkyne; this reaction will be described here.

The molecular ions $[RuR(CO)L'_2]^+$ (R = H or Ph and $L' = P^tBu_2Me$) with $BAr'_4{}^-$ counterion ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$) are apparent 14-electron species, which are lightly "stabilized" by two agostic ^tBu C−H groups, one from each L′.[2,3] As such, they are expected to bind Lewis bases, and we report here the reaction of $[RuH(CO)L'_2]^+$ with terminal alkynes. It will become apparent that the species $[RuR(CO)L'_2]^+$ are a source of *carbonyl-containing* species which are analogous to those introduced in the preceding paragraph. In essence, this work represents a comparison of the differences between isoelectronic species based on OsCl vs $Ru(CO)^+$.

Experimental Section

General. All reactions and manipulations were conducted using standard Schlenk and glovebox techniques under prepurified argon. Solvents were dried and distilled under nitrogen or argon and stored in airtight solvent bulbs with Teflon closures. All NMR solvents were dried, vacuum-transferred, and stored in a glovebox. ^1H, ^{19}F, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian Gemini 300 spectrometer. Chemical shifts are referenced to residual solvents peaks (^1H, $^{13}C\{^1H\}$) or external H_3PO_4 ($^{31}P\{^1H\}$) and $CFCl_3$ (^{19}F). $OsH_3Cl(P^iPr_3)_2$,[4] $OsHCl({=}C{=}CHSiMe_3)(P^iPr_3)_2$,[1] $RuH(OTf)(CO)(P^tBu_2Me)_2$,[3] and $NaBAr'_4$[5] were synthesized according to published procedures. $HC{\equiv}CSiMe_3$ (Oakwood) was distilled and degassed prior to use. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHNS/O analyzer at the Chemistry Department, Indiana University.

$OsCl\{(E)\text{-}CH{=}CHSiMe_3\}({=}C{=}CHSiMe_3)(P^iPr_3)_2$, 3. Method A. To a solution of $OsH_3Cl(P^iPr_3)_2$ (**1**) (100 mg, 0.18 mmol) in toluene (7 mL) was added $HC{\equiv}CSiMe_3$ (77 μL, 0.55 mmol). The resulting red solution was stirred for 12 h at room temperature. Then, the solution was filtered through Celite, and the volatiles were removed under vacuum, yielding a red solid. Yield: 95 mg (74%). Alternatively (**Method B**), this compound can be prepared by adding $HC{\equiv}CSiMe_3$ (22 μL, 0.155 mmol) to a solution of $OsHCl({=}C{=}CHSiMe_3)(P^iPr_3)_2$ (**2**) (100 mg, 0.155 mmol) in toluene (5 mL) and stirring at room temperature for 12 h. Yield: 81 mg (70%). Anal. Calcd for $C_{28}H_{63}ClOsP_2Si_2$: C, 45.23; H, 8.54. Found: C, 45.54; H, 7.98.

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† E-mail: eisenst@lsd.univ-montp2.fr.
‡ E-mail: caulton@indiana.edu.

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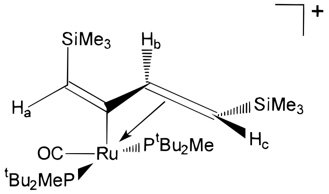
^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 20 °C): δ −0.11 (dt, $J_{\mathrm{P-H}} = 2.7$ Hz, $J_{\mathrm{H-H}} = 3.9$ Hz, 1H, $\mathrm{Os{=}C{=}C}H$), 0.09, 0.23 (both s, each 9H, $\mathrm{SiMe_3}$), 1.28 (dvt, $J_{\mathrm{H-H}} = 7.2$ Hz, $N = 12.6$ Hz, 18H, $\mathrm{PCH(C}H_3)_2$), 1.29 (dvt, $J_{\mathrm{H-H}} = 7.2$ Hz, $N = 13.2$ Hz, 18H, $\mathrm{PCH(C}H_3)_2$), 3.08 (m, 6H, $\mathrm{PC}H\mathrm{(CH_3)_2}$), 4.79 (dt, $J_{\mathrm{P-H}} = 2.1$ Hz, $J_{\mathrm{H-H}} = 13.5$ Hz, 1H, $\mathrm{Os{-}CH{=}C}H\mathrm{SiMe_3}$), 8.53 (dd, $J_{\mathrm{H-H}} = 3.9$ Hz, $J_{\mathrm{H-H}} = 13.5$ Hz, 1H, $\mathrm{Os{-}C}H\mathrm{{=}CHSiMe_3}$). ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{C_6D_6}$, 20 °C): δ −0.28 (s, $\mathrm{SiMe_3}$), 2.16 (s, $\mathrm{SiMe_3}$), 19.84, 20.14 (both s, $\mathrm{PCH(}C\mathrm{H_3)_2}$), 23.99 (t, $N = 11.8$ Hz, $\mathrm{P}C\mathrm{H(CH_3)_2}$), 87.19 (t, $J_{\mathrm{P-C}} = 2.5$ Hz, $\mathrm{Os{=}C{=}}C$), 130.87 (t, $J_{\mathrm{P-C}} = 2.8$ Hz, C_β vinyl), 153.99 (t, $J_{\mathrm{P-C}} = 7.2$ Hz, C_α vinyl), 272.33 (t, $J_{\mathrm{P-C}} = 9.6$ Hz, $\mathrm{Os{=}}C\mathrm{{=}C}$). ^{31}P{^{1}H} NMR (121 MHz, $\mathrm{C_6D_6}$, 20 °C): δ 14.1 (s). IR (Nujol, cm^{-1}): ν(C═C) 1593 (m), 1528 (m).

OsCl{C(CH═CHSiMe₃)═CHSiMe₃}(CO)₂(PⁱPr₃)₂, 4. A solution of $\mathrm{OsCl(CH{=}CHSiMe_3)({=}C{=}CHSiMe_3)(P^iPr_3)_2}$ (100 mg, 0.13 mmol) in toluene (7 mL) was frozen in liquid $\mathrm{N_2}$, the headspace of the Schlenk flask was evacuated, and excess CO (1 atm) was introduced. On warming to room temperature and stirring, the solution color changed from deep red to dark yellow. After stirring for 45 min, the volatiles were removed under vacuum, and pentane was added to give a yellow solution that was cooled at −40 °C, yielding white microcrystals. Yield: 43 mg (40%). Anal. Calcd for $\mathrm{C_{30}H_{63}ClO_2OsP_2Si_2}$: C, 45.06; H, 7.94. Found: C, 45.39; H, 7.67. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 20 °C): δ 0.25 (s, 9H, $\mathrm{SiMe_3}$), 0.34 (s, 9H, $\mathrm{SiMe_3}$), 1.05 (dvt, $J_{\mathrm{H-H}} = 6.6$ Hz, $N = 12.9$ Hz, 18H, $\mathrm{PCH(C}H_3)_2$), 1.33 (dvt, $J_{\mathrm{H-H}} = 6.9$ Hz, $N = 14.1$ Hz, 18H, $\mathrm{PCH(C}H_3)_2$), 2.69 (m, 6H, $\mathrm{PC}H\mathrm{(CH_3)_2}$), 5.31 (d, $J_{\mathrm{H-H}} = 18.3$ Hz, 1H, $\mathrm{Os{-}C(C}H\mathrm{{=}CHSiMe_3){=}CHSiMe_3}$), 7.01 (s, 1H, $\mathrm{Os{-}C(CH{=}CHSiMe_3){=}C}H\mathrm{SiMe_3}$), 7.43 (d, $J_{\mathrm{H-H}} = 18.3$ Hz, $\mathrm{Os{-}C(CH{=}C}H\mathrm{SiMe_3){=}CHSiMe_3}$). ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{C_6D_6}$, 20 °C): δ 0.86 (s, $\mathrm{SiMe_3}$), 1.94 (s, $\mathrm{SiMe_3}$), 19.36, 20.86 (both s, $\mathrm{PCH(}C\mathrm{H_3)_2}$), 24.25 (t, $N = 12.9$ Hz, $\mathrm{P}C\mathrm{H(CH_3)_2}$), 119.42 (s, $\mathrm{Os{-}C(CH{=}}C\mathrm{HSiMe_3){=}CHSiMe_3}$), 133.70 (t, $J_{\mathrm{P-C}} = 2.6$ Hz, $\mathrm{Os{-}C(CH{=}CHSiMe_3){=}}C\mathrm{HSiMe_3}$), 164.16 (s, $\mathrm{Os{-}C(}C\mathrm{H{=}CHSiMe_3){=}CHSiMe_3}$), 176.10 (t, $J_{\mathrm{P-C}} = 10.1$ Hz, $\mathrm{Os{-}C(CH{=}CHSiMe_3){=}CHSiMe_3}$), 179.84 (t, $J_{\mathrm{P-C}} = 7.2$ Hz, Os−CO), 182.99 (t, $J_{\mathrm{P-C}} = 7.2$ Hz, Os−CO). ^{31}P{^{1}H} NMR (121 MHz, $\mathrm{C_6D_6}$, 20 °C): δ 2.9 (s). IR (Nujol, cm^{-1}): ν(CO) 1998 (s), 1919 (s); ν(C═C) 1577 (m), 1525 (m). IR ($\mathrm{C_6D_6}$, cm^{-1}): ν(CO) 1998 (s), 1921 (s).

[Ru{η³-(Me₃Si)CH═C−CH═CH(SiMe₃)}(CO)(PᵗBu₂Me)₂][BAr′₄], 6. Method A. $\mathrm{RuH(OTf)(CO)(P^tBu_2Me)_2}$ (0.5 g, 0.83 mmol) and $\mathrm{NaBAr'_4}$ (0.73 g, 0.83 mmol) were mixed in fluorobenzene (10 mL) and stirred for 5 min. To the slurry was added $\mathrm{HC{\equiv}CSiMe_3}$ (0.25 mL, 1.8 mmol) via syringe. The orange color of the mixture immediately turned dark brown. The mixture was stirred for 30 min and filtered through a Celite pad. The residue was washed with fluorobenzene. The filtrate was evaporated to dryness to give a brown residue, which was recrystallized from fluorobenzene layered with pentane. Yield: 1.0 g (80%).



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Method B. $\mathrm{[RuH(CO)(P^tBu_2Me)_2][BAr'_4]}$ (10 mg, 7.6×10^{-3} mmol), **5**, was dissolved in $\mathrm{CD_2Cl_2}$ (0.5 mL). To this solution was added $\mathrm{HC{\equiv}CSiMe_3}$ (2.3 μL, 1.6×10^{-2} mmol) via syringe. The solution color changed immediately from orange to brown. ^{1}H and ^{31}P{^{1}H} NMR spectroscopies reveal clean formation of $\mathrm{[Ru\{\eta^3\text{-}(Me_3Si)CH{=}C{-}CH{=}CH(SiMe_3)\}(CO)(P^tBu_2Me)_2][BAr'_4]}$. Anal. Calcd for $\mathrm{C_{61}H_{67}BF_{24}OP_2RuSi_2}$: C, 48.77; H, 4.50. Found: C, 48.35; H, 4.80. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 20 °C): δ 0.34 (s, 9H, $\mathrm{SiMe_3}$), 0.43 (s, 9H, $\mathrm{SiMe_3}$), 1.15 (vt, $N = 13.5$ Hz, 18H, $\mathrm{P^tBu}$), 1.25 (vt, $N = 14.1$ Hz, 18H, $\mathrm{P^tBu}$), 1.62 (vt, $N = 5.1$ Hz, 6H, $\mathrm{PCH_3}$), 5.04 (dm, $J_{\mathrm{H-H}} = 2.1$ Hz, 1H, $\mathrm{H_a}$), 5.84 (d, $J_{\mathrm{H-H}} = 18$ Hz, 1H, $\mathrm{H_c}$), 6.10 (dm, $J_{\mathrm{H-H}} = 18$H, 1H, $\mathrm{H_b}$), 7.57 (br, s, *para*-H of $\mathrm{BAr'_4}$), 7.77 (br, s, 8H, *ortho*-H of $\mathrm{BAr'_4}$). ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CD_2Cl_2}$, 20 °C): δ −0.18 (s, $\mathrm{SiMe_3}$), 0.005 (s, $\mathrm{SiMe_3}$), 8.9 (vt, $N = 11.3$ Hz, $\mathrm{P}C\mathrm{H_3}$), 28.2 (s, $\mathrm{PC(}C\mathrm{H_3))}$), 29.4 (s, $\mathrm{PC(}C\mathrm{H_3))}$), 38.3 (vt, $N = 9$ Hz, $\mathrm{P}C\mathrm{Me_3}$), 39.9 (vt, $N = 9.1$ Hz, $\mathrm{P}C\mathrm{Me_3}$), 98.8 (s, $C\mathrm{H_c}$), 110.9 (s, $C\mathrm{H_b}$), 118.1 (m, 4-C of $\mathrm{BAr'_4}$), 125.2 (q, $J_{\mathrm{C-F}} = 271$ Hz, $C\mathrm{F_3}$), 128.4 (s, $C\mathrm{H_a}$), 129.1 (q of m, $J_{\mathrm{C-F}} = 40.2$ Hz, 3 and 5 C of $\mathrm{BAr'_4}$), 135.4 (s, 2 and 6 C of $\mathrm{BAr'_4}$), 163.9 (t, $\mathrm{Ru{-}}C\mathrm{{=}C}$), 204 (t, CO). ^{31}P{^{1}H}NMR (121 MHz, $\mathrm{CD_2Cl_2}$, 20 °C): δ 38.6 (s). ^{19}F NMR (282 MHz, $\mathrm{CD_2Cl_2}$, 20 °C): δ −62.0 (s). IR (Nujol, cm^{-1}): ν(CO) 1961.

Table 1. Crystallographic Data[d]

formula	$\mathrm{[C_{61}H_{75}BF_{24}OP_2RuSi_2]}$	$\mathrm{C_{28}H_{63}ClOsP_2Si_2}$
color	orange	red
cryst dimens (mm)	0.34 × 0.34 × 0.42	0.21 × 0.20 × 0.25
space group	$Pna2_1$	$P2_1$
cell dimens	(at −170 °C)	(at −170 °C)
a (Å)	24.056(2)	7.961(1)
b (Å)	18.440(2)	10.710(1)
c (Å)	15.789(1)	20.697(3)
β (deg)		90.10(1)
Z	4	2
volume	7003.85	1764.68
calcd density	1.421	1.399
wavelength[a]	0.710 69	0.710 69
mol wt	1510.22	743.58
linear abs coeff (cm^{-1})	4.1	38.61
min 2θ (deg)	6	6
max 2θ (deg)	45	45
no. of reflns collected	8430	2541
no. of unique intensities	4759	2453
no. of refined params	293	828
no. with $F > 0.0$	4658	2377
no. with $F > 2.33\sigma(F)$	4072	2178
R for averaging	0.047	0.019
final residuals		
$R(F)$[b]	0.0463	0.0277
$R_w(F)$[c]	0.0434	0.0255
goodness of fit for last cycle	1.878	1.207
max Δ/σ for last cycle	0.06	0.03

[a] Graphite monochromator. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$. [d] Diffractometer details: Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

X-ray Structure Determinations. (a) OsCl{(*E*)-CH═CHSiMe₃}-(═C═CHSiMe₃)(PⁱPr₃)₂. For $\mathrm{C_{28}H_{63}ClOsP_2Si_2}$ at −170 °C, $a = 7.961(1)$ Å, $b = 10.710(1)$ Å, $c = 20.697(3)$ Å, $\beta = 90.10(1)°$ with $Z = 2$ in space group $P2_1$; $R(F) = 0.0277$ for 2178 observed reflections. The X-ray quality crystals were grown by cooling a solution of the compound in pentane at −40 °C. A larger crystal was cleaved to obtain a suitable sized fragment, which was affixed to the end of a glass fiber using silicone grease. The mounted crystal was transferred to the goniostat, where it was cooled to −170 °C for characterization and data collection (Table 1). The data were collected using a standard moving crystal−moving detector technique with fixed backgrounds at each extreme of the scan. Data were corrected for Lorentz and polarization effects. Based on the measured dimensions of the crystal, an analytical absorption correction was applied and equivalent reflections averaged. Despite initial indications of orthorhombic symmetry, successful solution and refinement of the structure were only possible in a monoclinic setting. During refinement it became obvious that the vinyl and vinylidene ligands were mutually disordered. The four carbon atoms all refined to nonpositive definite thermal parameters when allowed to vary anisotropically. At this point hydrogen atoms were fixed, the four carbon atoms mentioned were refined isotropically, and all the other atoms were allowed to vary anisotropically. The final cycles of refinement consisted of fixed hydrogen atoms, isotropic parameters for the four disordered half-carbons bonded to the metal and two carbon atoms adjacent to the disorder, and

Table 2. Selected Bond Distances (Å) and Angles (deg) for $OsCl(CHCHSiMe_3)(CCHSiMe_3)(P^iPr_3)_2$

Os(1)–Cl(2)	2.416(3)	Os(1)–C(29)	1.82(3)
Os(1)–P(3)	2.397(5)	C(23)–C(24)	1.45(3)
Os(1)–P(13)	2.403(5)	C(29)–C(30)	1.32(3)
Os(1)–C(23)	1.92(3)		
Cl(2)–Os(1)–P(3)	88.3(3)	P(3)–Os(1)–C(29)	95(1)
Cl(2)–Os(1)–P(13)	88.2(3)	P(13)–Os(1)–C(23)	92(1)
Cl(2)–Os(1)–C(23)	121(1)	P(13)–Os(1)–C(29)	88(1)
Cl(2)–Os(1)–C(29)	141(1)	C(23)–Os(1)–C(29)	97(1)
P(3)–Os(1)–P(13)	176.5(1)	Os(1)–C(23)–C(24)	139(2)
P(3)–Os(1)–C(23)	90(1)	Os(1)–C(29)–C(30)	171(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Ru[(Me_3Si)CH{=}C{-}CH{=}CH(SiMe_3)](CO)(P^tBu_2Me)_2^+$ in its $B[C_6(CF_3)_2H_3]_4^-$ Salt

Ru(1)–P(2)	2.393(3)	Ru–C(26)	2.57(1)
Ru(1)–P(12)	2.499(3)	O(35)–C(34)	1.16(1)
Ru(1)–C(27)	2.28(1)	C(26)–C(27)	1.40(2)
Ru(1)–C(28)	2.01(1)	C(27)–C(28)	1.45(1)
Ru(1)–C(34)	1.84(1)	C(28)–C(29)	1.31(1)
Ru(1)–C(4)	2.943		
P(2)–Ru(1)–P(12)	159.70(9)	Ru(1)–P(2)–C(11)	112.8(3)
P(2)–Ru(1)–C(34)	90.0(3)	Ru(1)–P(12)–C(13)	115.5(3)
P(12)–Ru(1)–C(28)	101.6(3)	Ru(1)–P(12)–C(17)	117.9(3)
P(12)–Ru(1)–C(34)	85.5(3)	Ru(1)–P(12)–C(21)	106.1(3)
Ru(1)–P(2)–C(3)	99.6(3)		
Ru(1)–P(2)–C(7)	123.9(3)		

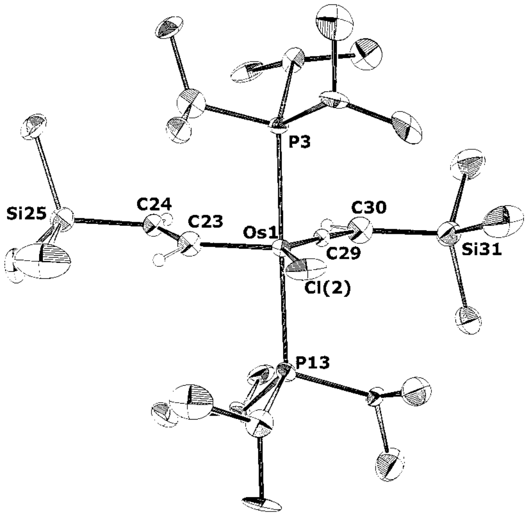

Figure 1. ORTEP drawing of $Os[CCH(SiMe_3)][CHCH(SiMe_3)]Cl(P^iPr_3)_2$. Only the vinyl and vinylidene hydrogens are shown.

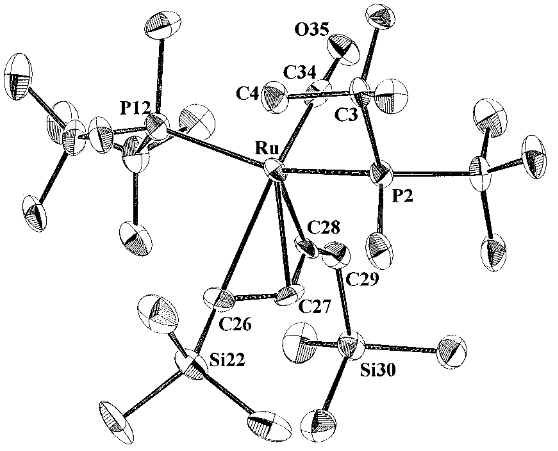

Figure 2. ORTEP drawing of the nonhydrogen atoms of $Ru[(Me_3Si)HC{=}C{-}CH{=}CH(SiMe_3)](CO)(P^tBu_2Me)_2^+$.

anisotropic parameters for the remaining atoms. The absolute configuration reported here refined to significantly lower residuals than its enantiomer. No significant changes in the structure were found in a purely isotropic refinement. A final difference Fourier was featureless, the largest peak being 1.21 e/A^3. Results of the structure determination are shown in Table 2 and Figure 1. We have refined the structure of OsCl(–CH=CHSiMe$_3$)(=CH=CHSiMe$_3$)(P^{i}Pr$_3$)$_2$ in the orthorhombic space group $P22_12_1$ (http://www.iumsc.indiana.edu/cgi-bin/getinfo.pl/98405). The results do not significantly change any of the structural parameters, and the molecule still suffers from the same disorder as reported in the $P2_1$ space group. The residual in $P2_1$ is lower ($R = 0.027$ vs 0.034). The fact remains that the beta angle is not 90°: it was determined to be 90.10(1)° based on two independent sets of data, and the diffractometer alignment was verified after the measurements were taken.

(b) $[Ru\{\eta^3\text{-}(Me_3Si)CH{=}C{-}CH{=}CH(SiMe_3)\}(CO)(P^tBu_2Me)_2][BAr'_4]$. For $C_{61}H_{75}BF_{24}OP_2RuSi_2$ at -178 °C, $a = 24.056(2)$ Å, $b = 18.440(2)$ Å, $c = 15.789(1)$ Å with $Z = 4$ in space group $Pna2_1$; $R(F) = 0.0463$ for 4072 observed data. The X-ray quality crystals were grown by layering the solution of the compound in CH_2Cl_2 with pentane at -20 °C. A well-formed orange crystal was pipetted from the recrystallization media, dried, and affixed to the end of a glass fiber using silicone grease. The crystal was then transferred to the goniostat, where it was cooled to -170 °C for characterization and data collection (Table 1). Standard inert atmosphere techniques were used during handling. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with orthorhombic symmetry corresponding to the space group $Pna2_1$ or $Pnam$. Subsequent solution and refinement confirmed the former choice. Data were collected using a continuous θ, 2θ scan with fixed background counts at each extreme of the scan. Equivalent data were averaged after Lorentz and polarization effects were applied. The structure was readily solved by direct methods (SHEXTL-PC) and standard Fourier techniques. Most hydrogen atoms were located in a difference Fourier phased on the nonhydrogen atoms and were included in the final least-squares refinement. Hydrogen atoms on several of the methyl groups did not converge properly, so all hydrogens were placed in fixed idealized positions, and only nonmethyl hydrogens were allowed to vary isotropically in the final refinement. A final difference Fourier was essentially featureless, the largest peaks being less than 0.6 e/A^3. Results of the structure determination are shown in Table 3 and Figure 2. When we refined the structure of the ruthenium compound with all carbons isotropic, to have a better data-to-parameter ratio (http://www.iumsc.indiana.edu/cgi-bin/getinfo.pl/98404), there were no significant differences (≤1 esd) in the structure.

Computational Details. Ab initio calculations were carried out with the Gaussian 94 set of programs within the framework of DFT at the B3LYP level.[6] LANL2DZ effective core potential (quasi relativistic for the metal centers) was used to replace the 28 innermost electrons of Ru, the 46 innermost electrons of Os, and the 10 core electrons of P, Cl, and Si. The LANL2DZ basis set was used for all atoms but the H of PH_3, which were represented at the STO-3G level. Polarization functions have been added only to all C and C-bonded H's. Full geometry optimization was performed with no symmetry restriction.

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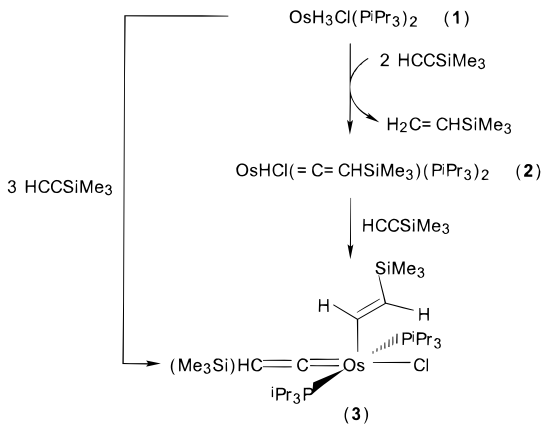
Scheme 1

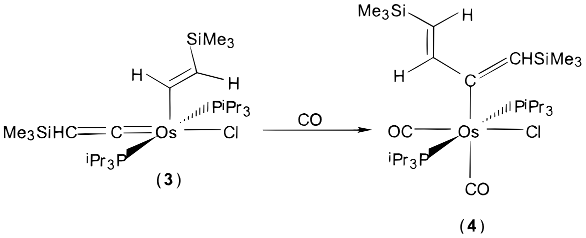


Results

Preparation and Characterization of OsCl{(*E*)-CH=CHSiMe$_3$}(=C=CHSiMe$_3$)(P^{i}Pr$_3$)$_2$, 3. Trimethylsilylacetylene inserts in the Os−H bond of OsHCl(=C=CHSiMe$_3$)(P^{i}Pr$_3$)$_2$ (**2**) giving the vinyl−vinylidene complex OsCl{(*E*)-CH=CHSiMe$_3$}(=C=CHSiMe$_3$)(P^{i}Pr$_3$)$_2$ (**3**). Alternatively, this compound can be prepared by reaction of OsH$_3$Cl(P^{i}Pr$_3$)$_2$ (**1**) with HC≡CSiMe$_3$ in a molar ratio 1:3 (Scheme 1). The ^{1}H NMR spectrum of **3** shows the peak corresponding to the proton on the β-carbon atom of the vinylidene ligand at −0.11 as a doublet of triplets by coupling with both phosphines and with the α-proton of the vinyl ligand (confirmed by means of a COSY experiment), and although this coupling through five bonds is unusual, long-distance coupling (up to nine bonds) can be observed in highly conjugated organic systems.[7] This proton is shifted to a very high field, as a consequence of the combination of the electron richness of the metal and the electron-donating group Me$_3$Si attached to the β-carbon atom of the vinylidene. The vinylic protons appear at 8.53 as a doublet of doublets (H$_\alpha$, coupling with the other vinylic proton and with the vinylidene proton) and 4.79 ppm as a doublet of triplets (H$_\beta$, coupling with both phosphines and the α-proton of the vinyl ligand). The ^{13}C{^{1}H} NMR spectrum displays, in addition to the signals corresponding to the phosphines, four triplets assigned to the vinylidene (272.33, 87.19 ppm, C$_\alpha$ and C$_\beta$, respectively) and vinyl (153.99, 130.87 ppm, C$_\alpha$ and C$_\beta$, respectively) carbon atoms. They appear in the typical range described before for these ligands and deserve no further comment.

The single-crystal X-ray structure of **3** reveals a distorted trigonal bipyramid (Y shape, considering the vinyl, vinylidene, and Cl ligands, Figure 1) with the phosphines in apical positions and the other three ligands on the equatorial plane. The majority of structurally characterized five-coordinate d^6 complexes with σ-donor and π-acceptor ligands are square-based pyramidal.[8] The Cl−Os−C(29) angle (141.5(11)°) is over 20° smaller than any basal angle in a square pyramid previously observed.[8] Due to the spatial similarity of both ligands, there is disorder between vinyl and vinylidene groups, but despite this, the Os−C(23)−C(24) (139(2)°) and Os−C(29)−C(30) (171(2)°) angles compare well with the ones found in other osmium−vinyl[8b,9] and osmium−vinylidene complexes.[10] Vinyl−vinylidene complexes have been proposed as intermediates in reactions of alkyne coupling[11] and also have been isolated in some cases.[12] As far as we know, compound **3** constitutes the first structurally characterized compound of this kind.

Preparation and Characterization of OsCl{C(CH=CHSiMe$_3$)=CHSiMe$_3$}(CO)$_2$(P^{i}Pr$_3$)$_2$, 4. Carbon monoxide induces migration of the vinyl ligand to the α-carbon atom of the vinylidene to give the vinyl derivative **4** (eq 2). The IR spectrum of **4** in C$_6$D$_6$ shows two CO stretching frequencies of similar intensity at 1998 and 1921 cm^{-1}, in accord with a *cis*-disposition of both ligands. ^{1}H NMR spectrum shows three resonances for the three vinylic protons at 5.31, 7.01, and 7.43 ppm. The ^{13}C{^{1}H} NMR spectrum shows, in addition to two triplets corresponding to the carbonyl ligands (179.84, 182.99 ppm), four peaks at 119.42, 133.70, 164.16, and 176.10 ppm assigned to the carbon atoms of the vinyl ligand by comparison with reported chemical shifts on related rhodium complexes.[12c]



(2)

Reaction of **3** with equimolar carbon monoxide yields a mixture of unreacted **3** and the dicarbonyl complex **4**. This means that any 1:1 CO adduct reacts more rapidly with CO than does **3** itself.

Reaction of [RuH(CO)(P^{t}Bu$_2$Me)$_2$][BAr′$_4$] (5) with Trimethylsilylacetylene. Addition of 2 equiv of HC≡CSiMe$_3$ to a CD$_2$Cl$_2$ solution of **5** causes an immediate color change from orange to deep brown. NMR analysis of the mixture reveals a clean reaction to give a product that shows only one broad ($\nu_{1/2}$ = 65 Hz) singlet in the ^{31}P{^{1}H} NMR spectrum and a sharp singlet in the ^{19}F NMR spectrum. In the vinyl region of the ^{1}H NMR spectrum there are three types of peaks with equal intensity at 6.10 (doublet of multiplets), 5.84 (doublet), and 5.04 ppm (doublet of multiplets). In the phosphine ^{t}Bu region two virtual triplets are seen at 1.25 and 1.15

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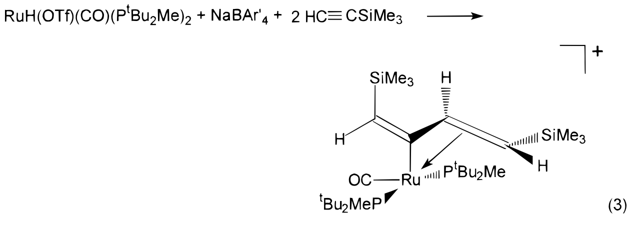
ppm, indicating that the two ^{t}Bu groups in the *trans* phosphine ligands are diastereotopic. In the $SiMe_3$ region two singlets with the same intensity are found at 0.34 and 0.43. Therefore, the organometallic product contains the coupled unit from two alkyne molecules. The definitive structure of the product comes from the X-ray crystal structure analysis (vide infra). Single crystals were grown from a CH_2Cl_2 solution of **6** (prepared more conveniently directly from $RuH(OTf)(CO)(P^tBu_2Me)_2$, $NaBAr'_4$, and $HC{\equiv}CSiMe_3$) layered with pentane (eq 3). The ORTEP diagram is depicted in Figure 2.

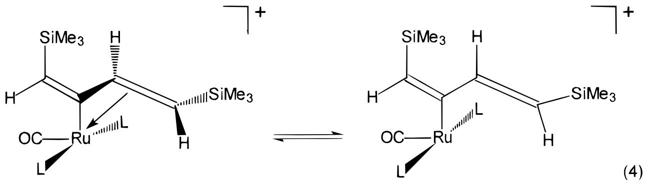


6

This shows that two alkynes have had one H added from Ru and they have been coupled through one carbon to give a butadienyl ligand $Me_3Si(H)C{=}CH{-}C{=}CH(SiMe_3)$; this ligand is η^3-bound to the Ru and can be thought of as occupying two coordination sites on the metal. One $=CH(SiMe_3)$ group does not interact with the metal. The geometry of this complex can be viewed as a distorted octahedron with one site occupied by an agostic interaction from the ^{t}Bu group of one phosphine ligand. The agostic Ru−C(4) distance is 2.943 Å. This agostic interaction shortens the Ru−P(2) bond (agostic) significantly (0.1 Å compared to the other Ru−P bond). Moreover, the Ru−P(2)−C(3) angle (99.6°) is compressed from the normal Ru−P−C angles (115°). These structural parameters are similar to those found in $RuH(CO)(P^tBu_2Me)_2^+$,[3] $RuPh(CO)(P^tBu_2Me)_2^+$,[2] and $Ir(H)_2(P^tBu_2Ph)_2^+$.[13] However, the Ru−C(4) distance (2.943 Å) is slightly longer than in the above formal 14 e$^-$ $RuH(CO)(P^tBu_2Me)_2^+$, suggesting marginally weaker agostic interaction. The strong deviation of linearity of the P−Ru−P angle (159.7°) could not be entirely due to the agostic interaction, since it may also be attributed to the steric repulsion between the Me_3Si of the butadienyl ligand and the ^{t}Bu groups of the phosphine ligands. *Trans* to C(4), the σ-bound butadienyl carbon (C(28)) is 2.013 Å away from Ru. This distance is much shorter than that of the π-coordinated ones (C(26) and C(27), 2.568 and 2.277 Å, respectively). Therefore, the complex is best viewed as a $\sigma-\pi$ allyl with the σ bond localized on C(28). Wakatsuki and co-workers reported a closely related complex, $RuCl\{\eta^3\text{-}Me_3SiCH{=}CCH{=}CHSiMe_3\}(CO)(PPh_3)_2$ (prepared from $RuHCl(CO)(PPh_3)_3$ and $Me_3SiC{\equiv}CCH{=}CHSiMe_3$).[14] In this complex, the butadienyl ligand also coordinates in σ,π mode with different bond lengths of Ru−C(σ) (2.044 Å) and RuC(π) (2.627 and 2.336 Å, respectively). These distances appear to be longer than that of **6** (0.04 Å for Ru−C(σ) and 0.06 Å for Ru−C(π)). Apparently, the formally 16-electron cationic complex, **6**, has a more electron-deficient Ru(II) center and thus binds ligands stronger. When the metal has a better back-donating ability, as in $Cp'Ru(L)(RR^1C{=}CR^2C{=}CR^3R^4)$ (Cp' = Cp or Cp*, L = phosphine), the butadienyl ligand is bonded to the metal more symmetrically (i.e., allyl).[15] The dihedral angle of the plane defined by the C(27)−C(28)−C(29) and the plane C(26)−C(27)−C(28) is 54.2°; therefore, the butadienyl ligand is twisted, as in other butadienyl complexes.[14,16]

Coupling of alkynyl (C_2R) and vinylidene (CCHR) ligands on Ru or Os has been reported earlier.[16−21] However, this gives an R_2HC_4 ligand, which is 2 H more oxidized than our $R_2H_3C_4$ ligands here (from vinylidene and vinyl). Comparisons are therefore limited.

The lack of symmetry of the butadienyl ligand destroys any symmetry relationship between the phosphorus nuclei, *even if* (as is reasonable) the agostic interaction is rapidly fluxional at 25 °C between the two phosphines. It is thus significant that the $^{31}P\{^1H\}$ NMR spectrum shows only a singlet at 25 °C. However, at −70 °C, the $^{31}P\{^1H\}$ NMR spectrum is an AM pattern (two doublets) with a $^2J_{P-P}$ of 203 Hz, consistent with a large angle P−Ru−P. Since the barrier to agostic fluxionality is expected to be very low, we attributed this decoalescence to freezing out of some fluxionality that gives the Ru/butadienyl unit mirror symmetry. We propose that this is the process in eq 4, which is conversion to the η^1-butadienyl, which is, in fact, conversion to an η^1-vinyl. Note that, throughout this rearrangement, the ^{t}Bu groups on the phosphine are predicted to remain diastereotopic; indeed they still show two ^{1}H NMR chemical shifts at 25 °C, when the fluxionality of eq 4 is fast.



Comparison. In summary, there is no C−C coupling in vinyl vinylidene complex **3**, although η^3 binding of the newly formed unsaturated ligand could give an acceptable electron count. However, coordination of CO to osmium triggers C−C coupling (i.e., vinyl carbon migration to the vinylidene C_α), but the resulting unsaturated ligand remains monohapto bonded to Os. Moreover, the five-coordinate η^1-hydrocarbon monocarbonyl complex does not remain unsaturated but adds a second CO to adopt a six-coordinate, saturated form.

In the case of the cationic ruthenium monocarbonyl, terminal alkyne inserts in the Ru−H bond, then couples to a second alkyne to form a complex with the *same* butadienyl ligand as in **4**, but now η^3-attached to Ru. Ruthenium is sufficiently electrophilic in its $[Ru\{\eta^3\text{-}Me_3SiHC{=}C{-}CH{=}CHSiMe_3\}(CO)(P^tBu_2Me)_2]^+$ form that one ^{t}Bu group is required to agostically donate to the

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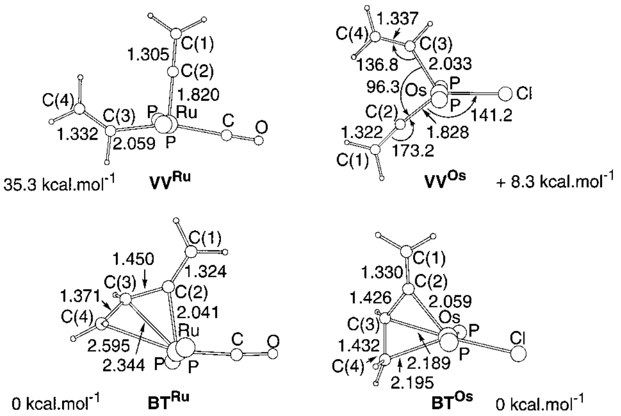

Figure 3. Optimized geometries and relative energies (kcal·mol^{-1}) for isomeric Ru and Os complexes; H's of PH$_3$ have been removed for clarity. See text for abbreviations.

metal, giving a "lightly stabilized" 18-electron complex. Obviously, **6** must be formed through a vinyl vinylidene intermediate similar to complex **3**.[22]

Computational Study. Optimization of Ru(CO)(C$_4$H$_5$)(PH$_3$)$_2$$^+$ and OsCl(C$_4$H$_5$)(PH$_3$)$_2$ reveals the existence of two minima, one of which has the structure of a vinyl vinylidene (**VV**) complex and the other has the structure of the butadienyl (**BT**) complex. For Ru(CO)$^+$, the **BT** isomer (**BT^{Ru}**) is more stable than the **VV** (**VV^{Ru}**) isomer by 35.3 kcal·mol^{-1}, while in the case of OsCl, **BT^{OS}** is more stable than **VV^{Os}** by only 8.3 kcal·mol^{-1}. The important feature of these calculations is that the marked preference for the butadienyl complex has decreased by 27 kcal·mol^{-1} on going from the Ru(CO)$^+$ group to the OsCl group. As will be apparent from the discussion of the geometries, the steric interactions from the phosphines will be considerably more important for the butadienyl complex, whose stability is thus overestimated by the modeling of the phosphine ligands as PH$_3$. The energy pattern thus reflects well that **VV^{Os}** and **BT^{Ru}** are the two experimentally observed structures.

The structures of **BT^{Ru}**, **BT^{Os}**, **VV^{Ru}**, and **VV^{Os}** are shown in Figure 3. Since the influence of silyl groups on the butadienyl structure was not clear, the structure of [Ru(CO){(H$_3$Si)C(H)=CH−C=C(H)(SiH$_3$)}(PH$_3$)$_2$]$^+$, **BT^{RuSi}**, has been optimized at the same level of theory as **BT^{Ru}**. Since no significant geometrical difference was obtained between **BT^{RuSi}** and **BT^{Ru}**, only the latter will be discussed.

The structure of **VV^{OS}** also agrees with the solid-state structure of **3** and shows the lack of significant influence of the disorder on the resolution of the geometry of **3** in the X-ray study. The vinyl and vinylidene groups both lie in the molecular mirror plane. The complex has a distorted trigonal bipyramidal geometry with a small angle between the vinylidene and the vinyl groups (C(2)−Os−C(3) = 96.3° which compares well to the experimental value (97.0°)). The chlorine is not symmetrically positioned with respect to the two ligands (C(2)−Os−Cl = 141.2° and C(3)−Os−Cl = 122.5°, compared with the experimental results, 141.5° and 121.4°, respectively). The vinyl Os−C(3)−C(4) angle is quite open (136.8°), and the vinylidene is slightly nonlinear (Os−C(2)−C(1) = 173.2°). The two phosphines are essentially *trans* to each other as they are in **3** (178.6°). It has been verified that rotating the vinyl group by 180° and thus putting the H of C(3) between the vinyl and vinylidene ligands does not create a minimum.

The agreement between the solid-state structure of **6** and the calculated **BT^{Ru}** model is also very good but will illustrate a larger influence of the steric factors between the butadienyl ligand and the large phosphine ligands used experimentally. The complex is a distorted octahedron with a missing site *trans* to C(2). The butadienyl ligand is η^3-bonded to the metal and is thus strongly twisted (C(1)−C(2)−C(3)−C(4) = 56.2° compared to the experimental 54.3°). The C(2) center is closer to the metal (Ru−C(2) = 2.041 Å), while the distance of C(3) and C(4) to the metal are 2.344 and 2.595 Å, respectively. Bond alternation is apparent in the butadienyl ligand (C(1)−C(2) = 1.324 Å, C(2)−C(3) = 1.450 Å, C(3)−C(4) 1.371 Å), which compares well to the experimental corresponding values, 1.309, 1.445, and 1.397 Å. As expected, coordination to the metal makes the C(3)−C(4) double bond longer than C(1)−C(2). However, C(3)−C(4) is shorter than the average distance found in coordinated double bonds, an additional proof of the weak coordination.[23] Since the butadienyl ligand is mostly bonded to the metal through the Ru−C(2) σ bond, one can view this complex as a 16-electron unsaturated species with a strong σ-donor ligand C(2) and a weaker donor C(3)−C(4) π bond. A square-pyramidal geometry with C(2) at the apical site of the pyramid is thus preferred. This strong bond to the center of the butadienyl ligand has already been addressed by ab initio calculations.[14]

Since the butadienyl ligand is considerably twisted, some part of it is close to the phosphine ligands. This induces geometrical distortions to decrease those repulsions. Thus, while the phosphines are essentially *trans* in **BT^{Ru}**, they are significantly moved away from linearity in the experimental complex (159.7°). The presence of SiH$_3$ on C(1) and C(4) in the model complex **BT^{RuSi}** is not sufficient to mimic the steric interactions since the calculated P−Ru−P angle there is equal to 173.8°. The bulk of the phosphine ligands are responsible for their deviation away from linearity.

The geometry of **BT^{Os}** shows a significant influence of the metal fragment on the bonding mode of the butadienyl fragment. The η^3 bonding mode is more apparent with almost equal distance between Os and C(2), C(3) and C(4). Thus, the system cannot now be

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considered as a 14-electron d^6 ML_4 complex weakly stabilized by an additional metal$-\pi$-bond interaction. It is a truly 16-electron complex, and its geometry is best understood by analogy with d^6 ML_5 considering that the allylic part of the butadienyl ligand is in fact a bidentate ligand donating σ and π electrons to the metal. Due to the presence of a π donor, the structure has a Y shape with almost equal Cl$-$Os$-$C(2) and Cl$-$Os$-$C(4) angles. The distances within the butadienyl fragment have also been modified with respect to $\mathbf{BT^{Ru}}$. The C(2)$-$C(3) and C(3)$-$C(4) are almost equal, which indicates full delocalization of the four electrons of the ligand. The dihedral angle C(4)$-$C(3)$-$C(2)$-$C(1) is 46.7°, which is close to that in $\mathbf{BT^{Ru}}$.

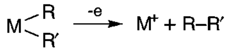
The structure of $\mathbf{VV^{Ru}}$ is also different from that of $\mathbf{VV^{OS}}$. As expected from the lack of π-donor ligand in a pentacoordinated d^6 ML_5 system, a square-pyramidal geometry is preferred for $\mathbf{VV^{Ru}}$. To prevent competition between the π-accepting capability of vinylidene and CO, these ligands go *cis* and the former ligand takes the apical site in $\mathbf{VV^{Ru}}$. There is no drastic difference in the geometry *within* the vinyl or the vinylidene between $\mathbf{VV^{Ru}}$ and $\mathbf{VV^{Os}}$.

What then is the reason for the large difference in energy between the two isomers for OsCl and $RuCO^+$ since all four are 16-electron complexes, which are either square-pyramidal or Y-shaped species?[24] Energy change from T to Y geometries involves a few kcal·mol^{-1} and cannot justify the big energy difference.[23,24] Thus, there is an intrinsic preference for making a C$-$C bond in the Ru complex, while there is an intrinsic preference for ligands with strong π-accepting capability in the case of Os. Os is a better electron donor and therefore prefers a structure with back-bonding capability. Ru is intrinsically a poorer donor, and its electron-donating ability is diminished by the presence of a π-acceptor ligand. A structure with more CC bonds is thus favored. This interpretation neglects the σ effects, which will involve comparing M$-$C bond energy to CC bond energies. Our point of view is probably a simplification of all of the effects. The calculations indicate, however, that the **BT** structure is favored, even for OsCl. It is clear that the lack of planarity of the butadienyl ligand induces large steric effects which are absent in the **VV** isomer. The small difference in energy between **VV** and **BT** in the case of OsCl is easily overcome by the steric factors, while the large difference in the case of $Ru(CO)^+$ permits the more sterically hindered structure to remain preferable.

The small difference in energy in the case of Os suggests that it should be possible to go from the **VV** structure to the **BT** structure. The activation barrier for intramolecular rearrangement has not been calculated, but related results for the transformation of Os hydrido carbyne into Os carbene complex involving the migration of H show it to be promoted by an incoming ligand.[25] This is the case also in the present study, since the addition of CO to $\mathbf{VV^{Os}}$ results in the coupling of C(2) and C(3). The complex does not stop at the $\mathbf{BT^{Os}}$ structure but incorporates one more CO to give product **4**.

Conclusion

Oxidatively induced reductive elimination (eq 5) is a



$$M\langle^{R}_{R'} \xrightarrow{-e} M^+ + R{-}R' \qquad (5)$$

reaction type of some generality, being the way a transformed organic ligand can be recovered from a transition metal (e.g., Ce^{IV} for arene complexes). Such oxidation can also be effected by olefins containing electron-withdrawing groups (e.g., tetracyanoethylene, esters, or acrylonitrile). The results reported here are qualitatively similar in that they represent reductive coupling (but not elimination from the coordination sphere), triggered by an electron-withdrawing ligand CO. In the absence of a carbonyl ligand, and influenced by the σ-donor ligand Cl, OsCl{(*E*)-CH=CHSiMe$_3$)(=C=CHSiMe$_3$)L$_2$ has no coupling of the two hydrocarbyl ligands and Os is in the oxidation state IV. In the case of the less easily oxidized 4d element Ru, and with a π-acid ligand CO (and thus a positive charge), reductive coupling occurs rapidly, to give the butadienyl ligand. For Os, coordination of two electron-withdrawing carbonyl ligands to **3** finally triggers reductive C$-$C coupling.

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Supporting Information Available: Full crystallographic data and bond lengths and angles for two compounds (16 pages). Ordering information is given on any current masthead page.

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