Alkylidene and Vinylidene "Pincer" Complexes from Reactions of Alkynes with Ruthenium and Osmium Hydrides

Dmitry G. Gusev,* Timothy Maxwell, Fedor M. Dolgushin,† Mikhail Lyssenko,† and Alan J. Lough‡

Department of Chemistry, Wilfrid Laurier University, Waterloo, Ontario, Canada N2L 3C5

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Reactions of 1-pentyne and *tert*-butylacetylene with RuHCl[1,3-$(CH_2PBu^t_2)_2C_6H_4$] and OsH_2-Cl(PCP) (PCP = [2,6-$(CH_2PBu^t_2)_2C_6H_3$]$^-$) afforded the square-pyramidal 16-electron alkylidene and vinylidene complexes RuCl(=C(Me)Pr)(PCP) (**1**), RuCl(=C=CHBu^t)[1-(C=CHBu^t)-2,6-$(CH_2PBu^t_2)_2C_6H_3$] (**2**), OsCl(=C=CHPr)(PCP) (**3**), and OsCl(=C=CHBu^t)(PCP) (**4**). These reactions were studied in solution by NMR spectroscopy. The structures of **1**−**4** were determined by X-ray crystallography.

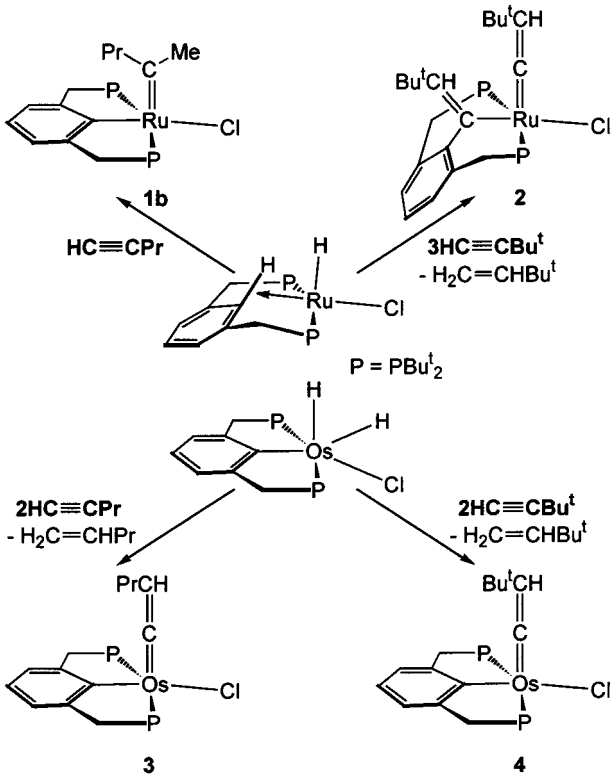
Introduction

Transition-metal complexes containing pincer-type ligands have attracted considerable interest due to their good thermal stability and some interesting structural and reactivity properties.[1] A series of ruthenium and osmium pincer complexes have been recently obtained in our group in reactions of the metal halides with 1,3-bis((di-*tert*-butylphosphino)methyl)benzene, 1,3-$(CH_2PBu^t_2)_2C_6H_4$.[2] We are currently studying the reactivity of the new species toward small molecules. Particularly, we have now investigated reactions of the hydrides RuHCl[1,3-$(CH_2PBu^t_2)_2C_6H_4$] and OsH_2Cl(PCP) (PCP = [2,6-$(CH_2PBu^t_2)_2C_6H_3$]$^-$) with representative terminal alkynes: 1-pentyne and *tert*-butylacetylene. This paper reports the structure of the four isolated products and some data on the mechanisms of their formation.

Results and Discussion

Preparation of Complexes 1−4. Reactions of RuHCl[1,3-$(CH_2PBu^t_2)_2C_6H_4$] and OsH_2Cl(PCP) with 1-pentyne and *tert*-butylacetylene are rapid at room temperature. Addition of 1 equiv of 1-pentyne to the ruthenium hydride resulted in formation of two isomers of the alkylidene complex RuCl(=C(Me)Pr)(PCP) (**1a** and **1b**, to be discussed below). Reaction of RuHCl[1,3-$(CH_2PBu^t_2)_2C_6H_4$] with *tert*-butylacetylene required 3 equiv of the alkyne and afforded the vinyl−vinylidene product RuCl(=C=CHBu^t)[1-(C=CHBu^t)-2,6-$(CH_2PBu^t_2)_2C_6H_3$] (**2**), according to Scheme 1. The osmium dihydride OsH_2Cl(PCP) could be quantitatively reacted with 2 equiv of both alkynes to give the corresponding vinylidene products OsCl(=C=CHPr)(PCP) (**3**) and OsCl(=C=CHBu^t)(PCP) (**4**). ^{1}H NMR spectra of the reaction solutions in C_6D_6 showed that formation of **2**−**4** was accompanied by production of 1 equiv of pentene (**3**) and 3,3-dimethylbutene (**2**, **4**). When we tried using smaller amounts of the alkynes, conversion of the starting hydrides was incomplete, and products **2**−**4** were formed

Scheme 1



* To whom correspondence should be addressed. E-mail: dgoussev@wlu.ca.

† Structural characterization of complexes **1** and **3**. Address: X-ray Laboratory, Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, Moscow B-334, Russia.

‡ Structural characterization of complexes **2** and **4**. Address: X-ray Laboratory, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

(1) Recent reviews: (a) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (b) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798. (c) Jensen, C. M. *Chem. Commun.* **1999**, 2443. (d) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 870.

(2) (a) Gusev, D. G.; Madott, M.; Dolgushin, F. M.; Lyssenko, K. A.; Antipin, M. Yu. *Organometallics* **2000**, *19*, 1734. (b) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Yu. *Organometallics* **2000**, *19*, 3429. (c) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Yu. *Organometallics* **2001**, *20*, 1001.

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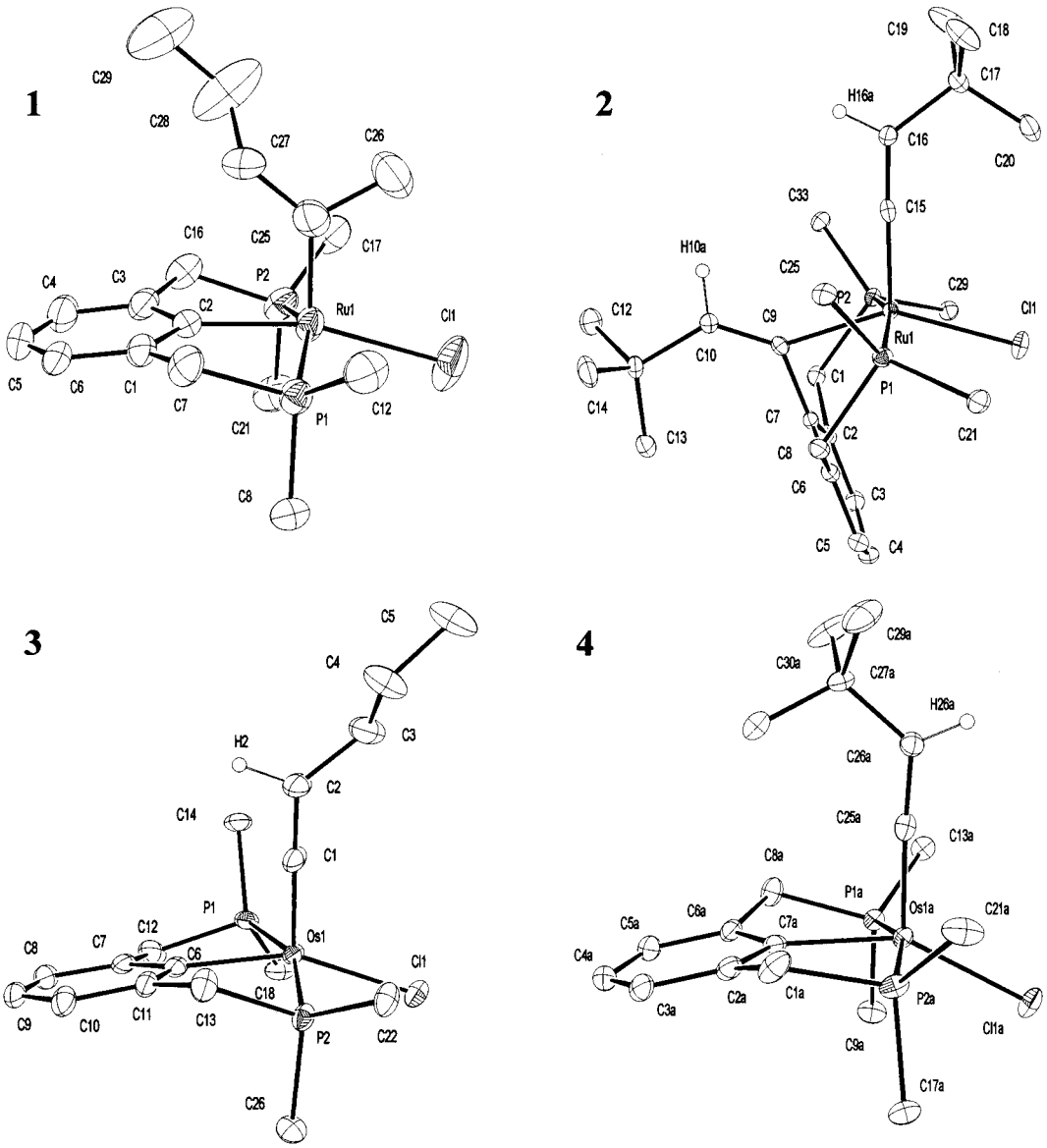


Figure 1. Partial molecular structures and atom-labeling schemes for complexes **1**−**4**. Thermal ellipsoids are at the 30% probability level. Most of the nonmetal hydrogens and methyl groups are omitted for clarity. One (A) of the two independent molecules is shown for complexes **3** and **4**.

along with some unidentified species observable by ^{31}P NMR spectroscopy.

The isolated ruthenium compounds are violet (**1**) and orange (**2**) air-stable solids. Osmium complexes **3** and **4** are black solids and are somewhat air-sensitive. Products **1**, **3**, and **4** are quite soluble in hydrocarbons and did not crystallize well from the reaction mixtures that limited the yields to 62−69%. Pure complex **2** is practically insoluble in common solvents.

Structural Characterization of Complexes 1−4. New compounds **1**−**4** were characterized by X-ray crystallography, NMR and IR spectroscopy, and elemental analysis (see the Experimental Section for details). The ^{13}C NMR spectra of **1**−**4** show the diagnostic shifts of the M=C carbon atoms at 342 (**1**), 323 (**2**), 275 (**3**), and 274 ppm (**4**). A characteristic feature of the vinylidene ligands in **2**−**4** is the high-field shift of the =CH protons: δ 3.29 (**2**), 0.89 (**3**), and 0.32 ppm (**4**). The crystal structures of complexes **1**−**4** are shown in Figure 1, and most of the important crystallographic data are collected in Tables 1 and 2. The four products possess distorted-square-pyramidal geometry, where the alkylidene and vinylidene ligands occupy the apical position. The P−P axis in **2**−**4** is perpendicular to the C=CHR (R = Pr, Bu^t) plane; thus, two C=CHR double-bond configurations are possible, with the C−H eclipsing the M−Cl or M−C bond (see Figure 1). Of the two double-bond isomers, only one was observed in the crystalline sample of **2**, whereas two isomers crystallized for complex **4** and were structurally characterized as independent molecules. Crystalline **3** also contains two independent molecules in the asymmetric unit, but we could not confirm that they were isomeric, because one molecule was disordered. All bonds and angles in **1**−**4** are normal. The metal−carbon distances are in the range 1.79−1.85 Å for the double bonds, while the single metal−carbon bonds are ca. 0.25 Å longer at 2.05−2.08 Å. The C=C bonds of the vinylidene ligands are in the range 1.32−1.33 Å.

NMR Study of Formation of Complexes 1, 2, and 4. This section describes the low-temperature NMR

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 1−4

complex **1**		complex **2**		complex **3**[a]		complex **4**[a]	
Ru−C(2)	2.051(7)	Ru−C(9)	2.055(3)	Os−C(6)	2.083(7)	Os−C(7)	2.073(4)
Ru−C(25)	1.849(8)	Ru−C(15)	1.795(3)	Os−C(1)	1.786(7)	Os−C(25)	1.810(4)
Ru−Cl(1)	2.492(3)	Ru−Cl(1)	2.423(1)	Os−Cl(1)	2.413(2)	Os−Cl(1)	2.401(1)
Ru−P(1)	2.400(3)	Ru−P(1)	2.441(1)	Os−P(1)	2.390(2)	Os−P(1)	2.376(1)
Ru−P(2)	2.393(3)	Ru−P(2)	2.453(1)	Os−P(2)	2.341(2)	Os−P(2)	2.390(1)
		C(15)−C(16)	1.321(4)	C(1)−C(2)	1.333(9)	C(25)−C(26)	1.328(6)
C(2)−Ru−Cl(1)	163.6(2)	C(9)−Ru−Cl(1)	146.75(7)	C(6)−Os−Cl(1)	155.6(2)	C(7)−Os−Cl(1)	149.4(1)
C(2)−Ru−P(1)	81.9(2)	C(9)−Ru−P(1)	83.19(7)	C(6)−Os−P(1)	81.6(2)	C(7)−Os−P(1)	82.3(1)
C(2)−Ru−P(2)	81.1(2)	C(9)−Ru−P(2)	82.80(7)	C(6)−Os−P(2)	80.8(2)	C(7)−Os−P(2)	82.1(1)
P(1)−Ru−P(2)	153.6(7)	P(1)−Ru−P(2)	163.53(3)	P(1)−Os−P(2)	160.11(6)	P(1)−Os−P(2)	161.54(4)
Cl(1)−Ru−P(1)	95.7(2)	Cl(1)−Ru−P(1)	93.53(3)	Cl(1)−Os−P(1)	98.12(6)	Cl(1)−Os−P(1)	93.26(4)
Cl(1)−Ru−P(2)	95.0(2)	Cl(1)−Ru−P(2)	93.44(3)	Cl(1)−Os−P(2)	94.00(6)	Cl(1)−Os−P(2)	95.18(4)
C(25)−Ru−P(1)	99.9(2)	C(15)−Ru−P(1)	96.25(8)	C(1)−Os−P(1)	97.2(2)	C(25)−Os−P(1)	95.0(1)
C(25)−Ru−P(2)	100.0(2)	C(15)−Ru−P(2)	95.86(8)	C(1)−Os−P(2)	92.6(2)	C(25)−Os−P(2)	95.54(1)
C(25)−Ru−Cl(1)	106.8(3)	C(15)−Ru−Cl(1)	107.43(8)	C(1)−Os−Cl(1)	112.4(2)	C(25)−Os−Cl(1)	117.7(1)
C(25)−Ru−C(2)	89.6(3)	C(15)−Ru−C(9)	105.8(1)	C(1)−Os−C(6)	91.7(3)	C(25)−Os−C(7)	92.9(2)
		C(16)−C(15)−Ru	178.2(2)	C(2)−C(1)−Os	178.47	C(26)−C(25)−Os	176.2(4)

[a] Data for one (A) of the two independent molecules.

Table 2. Crystallographic Data for Complexes 1−4

	1	**2**	**3**	**4**
formula	$C_{29}H_{53}ClP_2Ru$	$C_{36}H_{63}ClP_2Ru$	$C_{29}H_{51}ClP_2Os$	$C_{30}H_{53}ClP_2Os\cdot0.5C_6H_{14}$
fw	600.20	694.36	687.35	701.38
T, K	295	150	163	150
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	Cc	$P2_1/c$	$P\bar{1}$
a, Å	11.612(7)	18.5930(3)	19.096(3)	11.9714(2)
b, Å	16.812(9)	15.9030(3)	16.087(3)	15.0042(3)
c, Å	16.348(5)	12.1800(3)	21.630(3)	18.5714(3)
α, deg	90	90	90	84.1130(10)
β, deg	101.01(3)	91.7320(7)	114.319(3)	84.3670(10)
γ, deg	90	90	90	85.5490(10)
V, Å^3	3133(3)	3599.79(13)	6055.0(17)	3294.51(10)
Z	4	4	8	4
D(calcd), g/cm^3	1.272	1.281	1.451	1.457
abs coeff, mm^{-1}	0.703	0.621	4.418	4.067
total no. of rflns	5797	16148	94919	15062
no. of unique rflns	5508	7774	17689	11230
R,[a] %	5.78	2.95	5.87	3.43
R_w,[a] %	24.10	7.30	14.04	6.67

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

studies carried out to get some insights into the mechanisms of formation of complexes **1**, **2**, and **4**.

Representative $^{31}P\{^1H\}$ NMR spectra for the reaction between HC≡CBu^t and OsH_2Cl(PCP) are shown in Figure 2, and the structural interpretations are given in Scheme 2. The osmium dihydride reacted immediately with *tert*-butylacetylene at −80 °C in CD_2Cl_2 to give a monohydride product (^1H, δ −10.7, t, $^2J_{HP}$ = 14.0 Hz; ^{31}P, δ 40, doublet in the hydride-coupled spectrum). This product was stable between −80 and −60 °C. In addition to the hydride and the PCP ligand resonances, it showed an AB type system in the ^1H spectra between 2.2 and 3.1 ppm, with J_{AB} = 8.7 Hz. ^{13}C DEPT and {H,C} HETCOR experiments established that the AB resonances were due to two CH groups (^{13}C δ 164.0 and 138.0) and can be interpreted as a η^2-vinyl ligand of OsH(η^2-HC=CHBu^t)Cl(PCP) (**A**). Thus, the first detectable intermediate was the product of insertion of the alkyne into an Os−H bond.

When it was warmed to −40 °C, **A** decomposed by the loss of 3,3-dimethylbutene, as was evident from the proton spectra. One new intermediate (^{31}P δ 92.8) that appeared at this temperature could be interpreted as a η^2-HC≡CBu^t complex (**B**), on the basis of the observation of a low-field ^1H shift (δ 10.73, s, ≡C*H*) characteristic of a η^2-alkyne ligand.[3] Between −40 and −20 °C, **B** coexisted with two monohydride species (^{31}P, δ 47.0 and 21.3; ^1H, δ −9.0 and −9.23, t, $^2J_{HP}$ = 9.8 Hz,

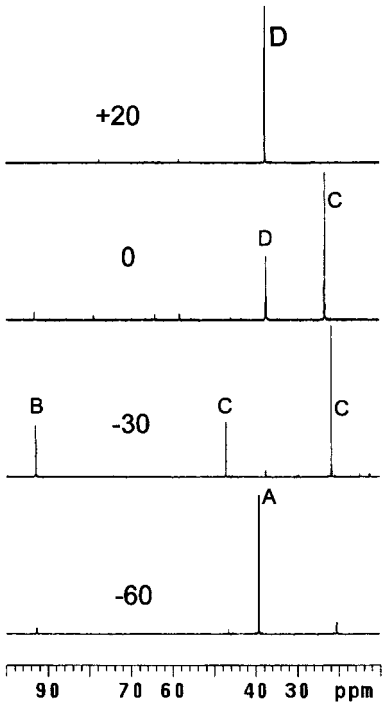
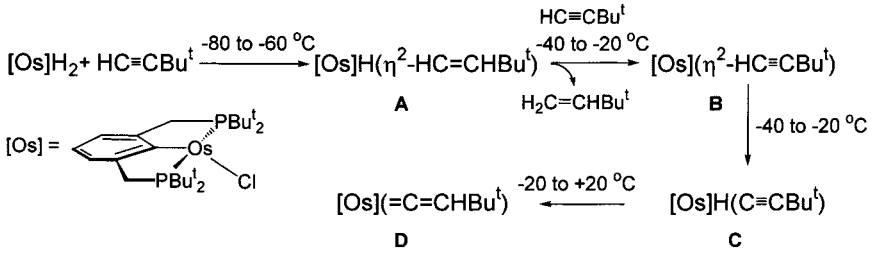


Figure 2. Representative low-temperature $^{31}P\{^1H\}$ NMR spectra for the reaction between HC≡CBu^t and OsH_2Cl(PCP).

assigned by selective ^{31}P decoupling). The two could be isomers of the hydrido alkynyl complex OsH(C≡CBu^t)-

(3) Caulton, K. G.; Renkema, K. B. *New J. Chem.* **1999**, *23*, 1027.

Scheme 2

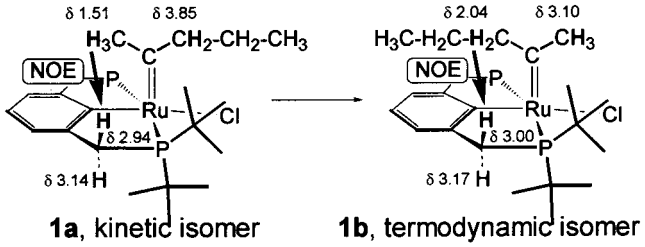


Cl(PCP) (**C**), formed by oxidative addition of the alkyne in **B**. In agreement with this interpretation, when deuterated DC≡CBu^t was reacted with $OsH_2Cl(PCP)$, the ^1H resonances of **B** and **C** at δ 10.73, −9.0, and −9.23 were not seen; i.e., the sites were deuterated. Further warming to 0 °C resulted in disappearance of **B** and conversion of the hydrido alkynyl species **C** to the vinylidene product **D** (complex **4**). The reaction of DC≡CBu^t afforded OsCl(=C=CDBu^t)(PCP) along with ^{t}BuCH≡CHD (cis/trans = 85/15). Our observations are in agreement with the mechanism of formation of a vinylidene ligand from a terminal alkyne involving η^2 coordination of the alkyne followed by oxidative addition of the H−C≡ bond to give a hydrido alkynyl compound, which finally rearranges to the vinylidene by migration of the metal-bonded hydrogen (1,3-hydrogen shift).[3,4]

The hydride RuHCl[1,3-$(CH_2PBu^t_2)_2C_6H_4$] reacted with HC≡CBu^t at −80 °C in CD_2Cl_2 to produce two intermediates resonating at δ 36 and 13 (62:38) in ^{31}P NMR. The former was a monohydride complex (^1H, δ −9.5, t, $^2J_{HP}$ = 6.6 Hz, assigned by selective ^{31}P decoupling), whereas the latter was a η^2-alkyne complex (^1H, δ 9.2, t, $^3J_{HP}$ = 1.3 Hz, ≡C*H*). When the temperature was raised, the ratio between the two intermediates decreased and the monohydride complex disappeared at −20 °C; the η^2-alkyne complex dominated the spectra at this temperature. Spectroscopic changes above −20 °C were difficult to interpret, since a broad resonance appeared at δ 34 in the ^{31}P spectra and some broad lines were observed in the proton spectra. We propose that the η^2-alkyne intermediate could rearrange into the vinylidene complex RuCl(=C=HBu^t)(PCP) and then undergo an intramolecular C−C coupling reaction between the vinylidene and the PCP ligand to give the vinyl intermediate RuCl[1-(C=CHBu^t)-2,6-$(CH_2PBu^t_2)_2$-C_6H_3]. This 14-electron intermediate presumably reacted with HC≡CBu^t to give the final product **2** at room temperature.

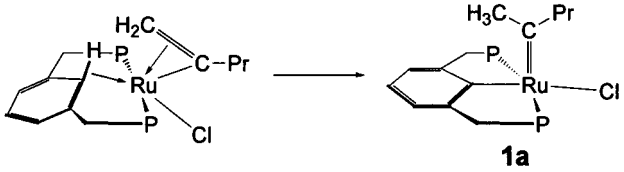
We finally studied a low-temperature reaction of RuHCl[1,3-$(CH_2PBu^t_2)_2C_6H_4$] and 1-pentyne in toluene-d_8. In this case, mixing reactants at −80 °C resulted in formation of three products: **1a** (67%, kinetic isomer, shown in Scheme 3; ^{31}P, δ 77), a η^2-alkyne complex (26%, likely Ru(η^2-HC≡CPr)Cl(PCP); ^{31}P, δ 16; ^{31}H, δ 9.4, ≡C*H*), and an unidentified minor intermediate (7%, ^{31}P, δ 6). The latter disappeared at −20 °C, leaving **1a** and the η^2-alkyne complex in a 3:1 ratio. At 0 °C, the η^2-alkyne complex started to disappear as well, and **1a** began to isomerize to the thermodynamic isomer **1b,** albeit very slowly. At room temperature, an equilibrium mixture of **1a** and **1b** (1:10) was formed within 1 h. The

Scheme 3. Isomers of 1[a]



[a] Only frontal H and Bu^t substituents on the PCP ligand are shown.

Scheme 4



fate of the η^2-alkyne intermediate is not clear. It could not be directly converted to **1**; however, the NMR spectra collected above 0 °C did not show any significant byproduct formation.

Complex **1a** was characterized by ^1H and ^{13}C NMR spectroscopy at 0 °C (see the Experimental Section for details). Particularly important for establishing the configuration of the double bond in the Ru=C(CH_3)-(C_3H_7) fragment of **1a** was the observation of NOE between the CH_3 group and the protons of the CH_2 groups of the PCP ligand (Scheme 3). For isomer **1b**, the NOE was observed between the CH_2 groups of the PCP ligand and the protons of the C_3H_7 group. The structural feature that makes **1b** more stable than **1a** is the arrangement of the −Pr group away from the bulky −Bu^t substituents on phosphorus.

Exclusive formation of **1a** at low temperature can be explained by insertion of HC≡CPr into the Ru−H bond of RuHCl[1,3-$(CH_2PBu^t_2)_2C_6H_4$], yielding an intermediate η^2-H_2C=CPr product.[5] If this intermediate has the H_2C= group in proximity of the agostic C−H, as shown in Scheme 4, the complex can undergo successive intramolecular C−H oxidative-addition and reductive-elimination reactions to give **1a**. We suggest that in the reaction of HC≡CBu^t the intermediate of the type shown in Scheme 4 is unfavorable and could not be produced in significant amounts, because it would have the bulky −Bu^t substituent placed in the crowded environment of the PBu^t_2 groups on phosphorus.

Comparison with Known Systems and Concluding Remarks. To put our data in context, it is interest-

(4) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Stegmann, R.; Frenking, G. *Organometallics* **1998**, *17*, 2089 and references therein.

(5) (a) This is similar to the insertion of HC=CPh into a Re−H bond of $[ReH_3(NO)(PPr^i_3)_2]^-$, which afforded $[ReH_2(H_2C=CPh)(NO)(PPr^i_3)_2]^-$.[5b] (b) Reinhart, B.; Gusev, D. G. *New J. Chem.* **1999**, *23*, 1.

Table 3. Reactions between Alkynes and Ruthenium and Osmium Hydride Complexes

hydride	alkyne	product (type)	byproduct[a]
$RuH_2Cl_2(PPr^i_3)_2$	HC≡CPh	$RuCl_2(=C=CHPh)(PPr^i_3)_2$ (**D**) (16 e)[6]	
$RuH(H_2)Cl(PBu^t_2Me)_2$	HC≡CSiMe$_3$	$RuHCl(=C=CHSiMe_3)(PBu^t_2Me)_2$ (**D**) (16 e)[7]	$H_2C=CHSiMe_3$
$RuH(H_2)Cl(PCy_3)_2$	HC≡CPh	$RuHCl(=C=CHPh)(PCy_3)_2$ (**D**) (16 e)[8]	$H_2C=CHPh$
$RuH_2(PMe_3)_4$	HC≡CPh	$RuH(C\equiv CPh)(PMe_3)_4$ (**C**) (18 e)[9]	$H_2C=CHPh$
$OsH_2Cl_2(PPr^i_3)_2$	HC≡CPh	$OsHCl_2(\equiv C-CH_2Ph)(PPr^i_3)_2$ (**E**) (18 e)[10]	
$OsH_2Cl_2(PPr^i_3)(\eta^1$-^{i}Pr$_2PC_2H_4NMe_2$)	HC≡CPh	$OsCl_2(=C=CHPh)(PPr^i_3)(\eta^2$-^{i}Pr$_2PC_2H_4NMe_2$) (**D**) (18 e)[11]	
$OsH_3Cl(PPr^i_3)_2$	HC≡CSiMe$_3$	$OsHCl(=C=CHSiMe_3)(PPr^i_3)_2$ (**D**) (16 e)[7]	
$OsH_3(\eta^2$-O$_2$CCH$_3$)$(PPr^i_3)_2$	HC≡CPh	$OsH(=C=CHPh)(\eta^2$-O$_2$CCH$_3$)$(PPr^i_3)_2$ (**D**) (18 e)[12]	
$OsH_2(\eta^2$-O$_2$CCH$_3$)[η^1-OC(O)CH$_3$]$(PPr^i_3)_2$	HC≡CCMe=CH$_2$	$OsH(\eta^2$-O$_2$CCH$_3$)[=C=CHCMe=CH$_2$]$(PPr^i_3)_2$ (**D**) (18 e)[13]	CH$_3$COOH
$[OsH_2(H_2O)(\eta^2$-O$_2$CCH$_3$)$(PPr^i_3)_2]^+$	HC≡CR (R = Ph, Bu^t)	$[OsH(\eta^2$-H$_2$CCPh)$(\eta^2$-O$_2$CCH$_3$)$(PPr^i_3)_2]^+$ (**A**) (18 e),[14] $OsH(\equiv CCH_2Bu^t)(\eta^2$-O$_2CCH_3$)$(PPr^i_3)_2]^+$ (**E**) (18 e)[14]	H_2O
$[OsH(H_2)(CO)(PPr^i_3)_2]^+$	HC≡CCO$_2$CH$_3$	$[Os\{C(=CH_2)C(\eta^1$-O)OCH$_3\}(CO)(PPr^i_3)_2]^+$ (**A**) (16 e)[15]	H_2
$OsCl_2(H_2)(CO)(PPr^i_3)_2$	HC≡CPh	$OsCl(CH=CHPh)(CO)(PPr^i_3)_2$ (**A**)[b] (16 e)[16]	HCl

[a] The byproduct is reported when specified in the publication. [b] This intermediate reacts further with HCl to give $OsCl_2(=CHCH_2Ph)(CO)(PPr^i_3)_2$.

ing to consider reactions of alkynes with ruthenium and osmium complexes having two or three metal-bonded hydrogens.[6−16] Such examples are collected in Table 3, and the products are assigned as vinyl (**A**), alkynyl (**C**), and vinylidene (**D**) type complexes, using the labeling of Scheme 2. Osmium hydrido alkylidyne derivatives are designated as **E**.

Our product **2** is related to the group of ruthenium complexes where formation of a vinylidene ligand is favorable on Ru(II) fragments [RuHClL$_2$] and [RuCl$_2$L$_2$]. The hydrido alkynyl form **C** is more stable, in combination with the electron-rich Ru(0) species [Ru(PMe$_3$)$_4$]. There is no example of the alkylidene complex Ru(=CMeR)L$_n$ obtained from the terminal alkyne HC≡CR; thus, the reactivity of RuHCl[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] toward HC≡CPr and the formation of **1** are unprecedented.

The osmium systems in Table 3 are diverse and show no particular structural preferences, apart from the tendency for higher coordination numbers and electronic saturation (18 electrons). It could be expected that the reactions of OsH$_2$Cl(PCP) with HC≡CR could produce the 18-electron hydrido alkylidyne derivatives OsHCl(≡CCH$_2$R)(PCP), analogous to the alkylidynes OsHCl$_2$(≡CCH$_2$R)$(PPr^i_3)_2$ (R = Ph, Cy) obtained by addition of HC≡CR to $OsH_2Cl_2(PPr^i_3)_2$. Apparently, alkyne hydrogenation is more facile in our system and the 16-electron vinylidene OsCl(=C=CHR)(PCP) products **3** and **4** are formed instead.

In conclusion, reactions of the new ruthenium and osmium complexes RuHCl[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] and OsH$_2$Cl(PCP) with terminal alkynes represent a synthetic approach to the preparation of compounds with metal−carbon double bonds. However, the composition and structure of the products are greatly influenced by the nature of the alkyne employed and might be very difficult to predict with any certainty in a general case of HC≡CR with a group R untested in this work.

Experimental Section

General Comments. All manipulations were performed under nitrogen in a drybox, where the anhydrous solvents were also stored and used. FT IR spectra were recorded on a Perkin-Elmer Spectrum BXII spectrometer. NMR measurements were done on a Varian UNITY Inova 300 spectrometer. Throughout this paper, the NMR data are reported with the apparent coupling of observed virtual triplets (vt) denoted as ^vJ. All J values are reported in Hz. Pentyne and *tert*-butylacetylene were purchased from Aldrich. The hydride complex OsH$_2$Cl[2,6-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_3$] was prepared according to a published method.[2c] RuHCl[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] was obtained using a modification of the reported approach,[2a] as follows.

Preparation of RuHCl[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$]. A mixture of [RuCl$_2$(*p*-cymene)]$_2$ (1.23 g, 2.01 mmol), 1,3-(CH$_2$PBu$^t_2$)C$_6$H$_4$ (1.66 g, 4.21 mmol), and 2,6-dimethylpyridine (lutidine) (0.43 g, 4.01 mmol) was stirred in 17 mL of 2-propanol under hydrogen for 48 h at 100 °C. Then the flask was purged with argon and a dark solid crystallized overnight at room temperature. It was filtered, washed with 3 × 3 mL of methanol, and dried under vacuum for 5 h. Yield: 1.83 g (86%). The isolated solid contained ca. 98% of RuHCl[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] according to the ^{31}P NMR spectrum, which also showed two peaks of unidentified species, both at ca. 1%. NMR spectroscopic and X-ray crystallographic data for the complex were reported.[2a] The product may contain a trace amount of the labile 18-electron dihydrogen complex Ru(H$_2$)$_2$Cl[2,6-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_3$], if crystallized under H$_2$. The H$_2$ ligand exchange between the dihydrogen complex and the main product can result in some broadening of the ^{1}H NMR spectra at ambient temperature.

Preparation of RuCl(=C(Me)Pr)[2,6-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_3$] (1). 1-Pentyne (38 mg, 0.56 mmol) was added to RuHCl[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] (280 mg, 0.53 mmol) in 5 mL of hexane. The reaction took place upon mixing, and the product precipitated. In 2 h, the precipitate was isolated by filtration, washed with 3 × 1.5 mL of hexane, and dried under vacuum. Yield: 210 mg (67%). Anal. Calcd for C$_{29}$H$_{53}$ClP$_2$Ru (600.20): C, 58.03; H, 8.90. Found: C, 58.14; H, 8.89. Isomer **1a**: ^{1}H{^{31}P} NMR

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(tol-d_8, 0 °C) δ 0.98 (t, $^3J_{HH}$ = 7.2, 3H, CH_3, Pr), 1.17 (s, 18H, CH_3), 1.23 (s, 18H, CH_3), 1.51 (s, 3H, CH_3), 1.62 (m, 2H, CH_2, Pr), 2.94 (d, $^2J_{HH}$ = 16.8, 2H, CH_2), 3.14 (d, 2H, CH_2), 3.85 (m, 2H, CH_2, Pr), 6.93 (t, $^3J_{HH}$ = 7.5, 1H, C$_6H_3$), 7.08 (d, 2H, C$_6H_3$) ^{31}P{^{1}H} NMR (tol-d_8, 0 °C) δ 77.1; ^{13}C{^{1}H} NMR (tol-d_8, 0 °C) δ 14.9 (s, *C*H$_3$, Pr), 21.0 (s, *C*H$_2$, Pr), 29.7 (vt, ^vJ = 2.6, *C*H$_3$), 30.7 (vt, ^vJ = 2.3, *C*H$_3$), 34.1 (vt, ^vJ = 10.5, *C*H$_2$), 35.6 (vt, ^vJ = 6.3, P*C*), 36.3 (vt, ^vJ = 7.1, P*C*), 45.2 (s, *C*H$_3$), 67.6 (s, *C*H$_2$, Pr), 121.4 (s, *C*H, Ar), 121.6 (vt, ^vJ = 8.1, *C*H, Ar), 151.2 (vt, ^vJ = 7.5, *C*, Ar), 180.0 (t, $^2J_{CP}$ = 3.8, Ru*C*), 340.0 (t, $^2J_{CP}$ = 7.2, Ru=*C*). Isomer **1b**: ^{1}H NMR (CD$_2$Cl$_2$) δ 0.55 (t, $^3J_{HH}$ = 7.2, 3H, CH_3, Pr), 1.25 (m, 2H, CH_2, Pr), 1.22 (vt, ^vJ = 6.1, 18H, CH_3), 1.28 (vt, ^vJ = 6.6, 18H, CH_3), 1.98 (m, 2H, CH_2, Pr), 3.02 (t, $^3J_{HP}$ = 1.5, 3H, CH_3), 3.14 (dvt, $^2J_{HH}$ = 17.1, ^vJ = 3.9, 2H, CH_2), 3.38 (dvt, ^vJ = 5.7, 2H, CH_2), 6.67 (t, $^3J_{HH}$ = 7.5, 1H, C$_6H_3$), 6.97 (d, 2H, C$_6H_3$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 78.1; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 16.8 (s, *C*H$_3$, Pr), 22.5 (s, *C*H$_2$, Pr), 32.1 (vt, ^vJ = 2.4, *C*H$_3$), 33.2 (vt, ^vJ = 2.2, *C*H$_3$), 36.1 (vt, ^vJ = 10.6, *C*H$_2$), 39.0 (vt, ^vJ = 7.2, P*C*), 39.2 (vt, ^vJ = 6.6, P*C*), 53.6 (s, *C*H$_3$), 65.9 (s, *C*H$_2$, Pr), 123.3 (t, $^4J_{CP}$ = 0.8, *C*H, Ar), 123.7 (vt, ^vJ = 8.1, *C*H, Ar), 154.1 (vt, ^vJ = 7.4, *C*, Ar), 180.2 (t, $^2J_{CP}$ = 3.5, Ru*C*), 341.8 (t, $^2J_{CP}$ = 6.9, Ru=*C*).

Preparation of RuCl(=C=CHBu^t)[1-(C=CHBu^t)-2,6-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_3$] (2). *tert*-Butylacetylene (482 mg, 5.87 mmol) was added to RuHCl[1,3-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_4$] (1.04 g, 1.95 mmol) in 30 mL of THF, and the reaction mixture was left overnight at room temperature. An orange solid precipitated; it was isolated by filtration, washed with 6 mL of THF, and dried under vacuum for 8 h. Yield: 954 mg (70%). Anal. Calcd for C$_{36}$H$_{63}$ClP$_2$Ru (694.36): C, 62.27; H, 9.15. Found: C, 62.24; H, 9.17. IR (Nujol): $\nu_{C=C}$ 1627 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.87 (s, 9H, CH_3), 1.13 (s, 9H, CH_3), 1.2, 1.3, 1.6 (broad, total 18H, CH_3), 1.48 (vt, ^vJ = 6.1, 18H, CH_3), 2.59 (dvt, $^2J_{HH}$ = 13.8, ^vJ = 3.9, 2H, CH_2), 3.29 (t, $^4J_{HP}$ = 3.3, 1H, =C*H*), 3.40 (dvt, ^vJ = 4.7, 2H, CH_2), 4.75 (t, $^4J_{HP}$ = 2.0, 1H, =C*H*), 6.93 (d, ^3J = 7.5, 2H, C$_6H_3$), 7.22 (t, 1H, C$_6H_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 37.5. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 27.4 (vt, ^vJ = 7.4, *C*H$_2$), 30.1 (s, *C*H$_3$), 31.1 (vt, ^vJ = 1.6, *C*H$_3$), 31.6 (t, $^4J_{CP}$ = 1.9, *C*(CH$_3$)), 31.8 (broad, *C*H$_3$), 33.0 (t, $^5J_{CP}$ = 1.2, *C*H$_3$), 38.2 (t, $^4J_{CP}$ = 1.0, *C*(CH$_3$)), 38.8 (vt, ^vJ = 4.3, P*C*), 39.3 (vt, ^vJ = 4.5, P*C*), 119.4 (t, $^3J_{CP}$ = 5.8, =*C*H), 122.5 (t, J_{CP} = 5.0, *C*, Ar), 127.4 (vt, ^vJ = 4.2, *C*H, Ar), 129.6 (t, $^4J_{CP}$ = 1.5, *C*H, Ar), 139.1 (t, $^3J_{CP}$ = 4.0, =*C*H), 142.5 (s, *C*, Ar), 157.8 (t, $^2J_{CP}$ = 9.5, Ru*C*), 322.8 (t, $^2J_{CP}$ = 14.1, Ru=*C*).

Preparation of OsCl(=C=CHPr)[2,6-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_3$] (3). 1-Pentyne (112 mg, 1.64 mmol) was added to OsH$_2$Cl[2,6-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_3$] (0.5 g, 0.80 mmol) in 3 mL of hexane. In 2 h, the reaction solution was filtered and then evaporated to dryness. The sticky residue was redissolved in 3 mL of ethanol. The product precipitated after 24 h at −30 °C. The solid was isolated by filtration, washed with 3 × 1.5 mL of ethanol, and dried under vacuum. Yield: 340 mg (62%). Anal. Calcd for C$_{29}$H$_{51}$ClP$_2$Os (687.35): C, 50.67; H, 7.48. Found: C, 50.84; H, 7.40. IR (Nujol): $\nu_{C=C}$ 1639, 1649 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.73 (t, $^3J_{HH}$ = 7.3, 3H, CH_3), 0.89 (tt, $^3J_{HH}$ = 7.1, $^4J_{HP}$ = 3.0, 1H, =C*H*), 1.14 (m, 2H, CH_2, Pr), 1.20 (vt, ^vJ = 6.1, 18H, CH_3), 1.53 (vt, ^vJ = 6.6, 18H, CH_3), 2.44 (m, 2H, CH_2, Pr), 3.50 (dvt, $^2J_{HH}$ = 16.8, ^vJ = 3.9, 2H, CH_2), 3.61 (dvt, ^vJ = 4.2, 2H, CH_2), 6.94 (t, $^3J_{HH}$ = 7.5, 1H, C$_6H_3$), 7.19 (d, 2H, C$_6H_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 42.1. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 14.0 (s, *C*H$_3$, Pr), 19.5 and 25.8 (t, J_{CP} = 1.7 and 1.2, *C*H$_2$, Pr), 30.3 (vt, ^vJ = 1.9, *C*H$_3$), 30.4 (vt, ^vJ = 2.0, *C*H$_3$), 37.7 (vt, ^vJ = 8.1, P*C*), 38.3 (vt, ^vJ = 13.0, *C*H$_2$), 38.9 (vt, ^vJ = 9.5, P*C*), 104.3 (t, $^3J_{CP}$ = 4.1, =*C*H), 121.1 (vt, ^vJ = 6.9, *C*H, Ar), 125.9 (t, $^4J_{CP}$ = 1.1, *C*H, Ar), 154.2 (vt, ^vJ = 6.9, *C*, Ar), 158.9 (t, $^2J_{CP}$ = 0.9, Os*C*), 274.9 (t, $^2J_{CP}$ = 9.6, Os=*C*).

Preparation of OsCl(=C=CHBu^t)[2,6-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_3$] (4). *tert*-Butylacetylene (133 mg, 1.62 mmol) was added to OsH$_2$Cl[2,6-(CH$_2$PBu$^t_2$)$_2$C$_6$H$_3$] (0.5 g, 0.80 mmol) in 15 mL of THF. In 2 h, the solution was evaporated to dryness. The residue crystallized upon triturating with 3 mL of ethanol. The solid was isolated by filtration, washed with 3 × 1.5 mL of ethanol, and dried under vacuum. Yield: 365 mg (65%). Anal. Calcd for C$_{30}$H$_{53}$ClP$_2$Os (701.37): C, 51.37; H, 7.62. Found: C, 51.22; H, 7.64. IR (Nujol): $\nu_{C=C}$ 1632 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.32 (t, $^4J_{HP}$ = 2.8, 1H, =C*H*), 0.86 (s, 9H, CH_3), 1.19 (vt, ^vJ = 6.0, 18H, CH_3), 1.56 (vt, ^vJ = 6.6, 18H, CH_3), 3.52 (dvt, $^2J_{HH}$ = 16.8, ^vJ = 4.1, 2H, CH_2), 3.61 (dvt, ^vJ = 4.1, 2H, CH_2), 6.92 (t, $^3J_{HH}$ = 7.2, 1H, C$_6H_3$), 7.17 (d, 2H, C$_6H_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 37.7. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 27.4 (t, $^4J_{CP}$ = 1.4, *C*(CH$_3$)), 30.6 (vt, ^vJ = 1.8, *C*H$_3$), 31.0 (vt, ^vJ = 2.0, *C*H$_3$), 33.3 (t, $^5J_{CP}$ = 1.0, *C*H$_3$), 38.2 (vt, ^vJ = 12.6, *C*H$_2$), 38.3 (vt, ^vJ = 7.8, P*C*), 38.9 (vt, ^vJ = 9.6, P*C*), 116.9 (t, $^3J_{CP}$ = 4.1, =*C*H), 121.1 (vt, ^vJ = 6.8, *C*H, Ar), 126.0 (t, $^4J_{CP}$ = 1.0, *C*H, Ar), 154.4 (vt, ^vJ = 6.6, *C*, Ar), 159.2 (t, $^2J_{CP}$ = 1.0, Os*C*), 274.2 (t, $^2J_{CP}$ = 9.2, Os=*C*).

Low-Temperature NMR-Tube Reactions. In a typical preparation, a 20 mg sample of one of the hydride complexes was dissolved in 0.4 mL of a deuterated solvent (CD$_2$Cl$_2$ or toluene-d_8) in a 5 mm NMR tube fitted with a PTFE valve. A solution of the required (according to the stoicheometry in Scheme 1) amount of 1-pentyne or *tert*-butylacetylene in 0.25 mL of the same solvent was condensed into the tube under vacuum, and then the tube was sealed. The two solutions were mixed by shaking, keeping the sample portion of the tube in cold (−80 °C) ethanol. The sample was inserted into a precooled probe, and the NMR measurements were started at −80 °C.

Crystal Structures. Complexes **1**−**3** were crystallized from diethylene glycol diethyl ether (1-Ethoxy-2-(2-ethoxy-ethoxy)-ethane). Crystals of **4** were obtained from hexane. Selected crystallographic data for **1**−**4** are reported in Tables 1 and 2; the structures are shown in Figure 1. All details for the crystallographic analyses of **1**−**4** are available in the Supporting Information.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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