Phosphine Ligand Effects on the Formation, Equilibration, and Reactivity of the Isomeric Vinyl Complexes (μ-H)$Os_3(CO)_9(PR_3)(\mu$-η^2-CH=CH_2)

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Received January 13, 1998

The equilibrium between the two structural isomers of the cluster compound (μ-H)$Os_3(CO)_9(L)(\mu$-η^2-CH=CH_2), previously observed for L = $P(C_6H_5)_3$, has been further studied for L = $P(C_2H_5)_3$, P(*p*-$CH_3OC_6H_4)_3$, P(*p*-$CH_3C_6H_4)_3$, and $P(C_6H_{11})_3$. The equilibrium constants vary with ligand size: 0.20 for L = $P(C_2H_5)_3$; 0.45 for L = P(*p*-$CH_3OC_6H_4)_3$, P(*p*-$CH_3C_6H_4)_3$, and $P(C_6H_5)_3$; and 2.20 for L = $P(C_6H_{11})_3$. These values demonstrate increasing preference for positioning the vinyl group remote from rather than adjacent to the phosphine ligand. The half-life for approaching equilibrium from a pure sample of the adjacent isomer also varies in the same order: $P(C_2H_5)_3$ (48 min), $P(C_6H_5)_3$ (83 min), and $P(C_6H_{11})_3$ (570 min). Analysis of selectively deuterated (μ-D)$Os_3(CO)_9(P(C_6H_5)_3)(\mu$-$\eta^2$-CH=CHD) shows that the C−D bond of the vinyl group is cis to the Os−C bond in the adjacent isomer but trans in the remote isomer. Removal of a carbonyl ligand from (μ-H)$Os_3(CO)_9(P(C_6H_5)_3)(\mu$-$\eta^2$-CH=$CH_2$) by trimethylamine oxide occurs selectively from the adjacent isomer to produce the vinylidene compound (μ-H)$_2Os_3(CO)_8(P(C_6H_5)_3)(\mu_3$-$\eta^2$-C=$CH_2$).

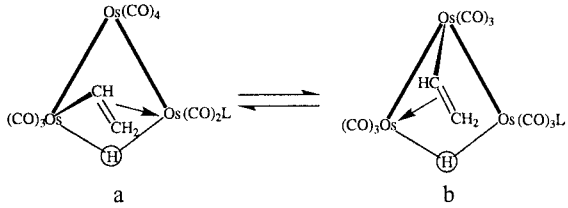
Introduction

One of the earliest reactions demonstrated for the formally unsaturated cluster compound (μ-H)$_2Os_3(CO)_{10}$ was its reaction with acetylene to give the vinyl compound (μ-H)$Os_3(CO)_{10}(\mu$-η^2-CH=CH_2).[1] Subsequent work with the derivatives (μ-H)$_2Os_3(CO)_9(PR_3)$ showed that analogous reactions with acetylene formed two isomeric vinyl derivatives.[2] However, the structures of these isomers were not established until our recent report of X-ray crystallographic and NMR spectroscopic studies of the triphenylphosphine derivatives (μ-H)$Os_3(CO)_9(PPh_3)(\mu$-η^2-CH=CH_2) (**1a**,**b**), which were also shown to equilibrate with each other (see Scheme 1).[3]

In this paper we show that the position of this equilibrium is dominated by the steric effects of the phosphine ligand. Specifically, increasing the steric bulk of the phosphine ligand shifts the equilibrium from favoring the adjacent isomer **a** toward favoring the remote isomer **b**. Furthermore, the rate of approach to equilibrium decreases as the phosphine ligand becomes more sterically demanding. Illumination of the rearrangement mechanism is provided by examination of the selectively deuterated compound (μ-D)$Os_3(CO)_9(P(C_6H_5)_3)(\mu$-$\eta^2$-CH=CHD), for which the ^{1}H NMR spectrum shows that isomer **1a**-d_2 has the vinylic deuterium atom cis to the Os−C σ bond (*Z*) but that it is positioned trans (*E*) in isomer **1b**-d_2.

Additionally, we demonstrate that loss of a carbonyl ligand from (μ-H)$Os_3(CO)_9(PPh_3)(\mu$-η^2-CH=CH_2) to form

Scheme 1



a single isomer of the vinylidene compound, (μ-H)$_2Os_3(CO)_8(PPh_3)(\mu_3$-$\eta^2$-C=$CH_2$), occurs selectively from isomer **1a**.

Experimental Section

Materials and Methods. All reactions were carried out under a nitrogen atmosphere. *n*-Hexane was distilled from sodium/benzophenone. Dichloromethane was distilled from calcium hydride. Trimethylamine oxide was purchased from Aldrich Chemical Co. and was sublimed twice prior to use. The compounds (μ-H)$_2Os_3(CO)_9(PR_3)$ were prepared by literature methods.[4] The derivatives (μ-H)$Os_3(CO)_9(PR_3)(\mu$-η^2-CH=CH_2) (R = *p*-$CH_3OC_6H_4$, *p*-$CH_3C_6H_4$, C_6H_{11}) were prepared analogously to (μ-H)$Os_3(CO)_9(PPh_3)(\mu$-η^2-CH=CH_2) from (μ-H)$_2Os_3(CO)_9(PR_3)$ and acetylene.[2] The labeled compound (μ-D)$Os_3(CO)_9(PPh_3)(\mu$-η^2-CH=CHD) was prepared in a similiar manner using (μ-D)$_2Os_3(CO)_9(PPh_3)$. Infrared spectra were obtained on a Perkin-Elmer 1750 FT-IR spectrometer. A Varian Unity 500 MHz spectrometer was used to obtain ^{1}H NMR spectra. Microanalyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences.

(μ-H)$Os_3(CO)_9(P(p$-$CH_3C_6H_4)_3)(\mu$-η^2-CH=CH_2) (2a,b). Anal. Calcd for $C_{32}H_{25}O_9Os_3P$: C, 33.27; H, 2.18. Found: C, 33.63; H, 2.49. IR (cyclohexane): ν(CO) 2090 m, 2069 w, 2059 w, 2045 s, 2032 w, 2005 vs, 1986 m, 1968 w, 1955 w cm^{-1}. ^{1}H

(1) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.
(2) Brown, S. C.; Evans, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1049.
(3) Koike, M.; Hamilton, D. H.; Wilson, S. R.; Shapley, J. R. *Organometallics* **1996**, *15*, 4930.
(4) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *114*, 313.

S0276-7333(98)00015-6 CCC: $15.00
Publication on Web 06/11/1998

Table 1. Ligand and Vinyl Isomer Equilibration Data

cmpd	ligand	θ (deg)[a]	pK_a[a]	K_{eq}[b]	k_1 (min^{-1})[c]	k_{-1} (min^{-1})[c]	$t_{1/2}$ (min)
6	$P(CH_3)_3$	118	8.65	<0.02			
5	$P(C_2H_5)_3$	132	8.69	0.20	$2.5(3) \times 10^{-3}$	$1.2(1) \times 10^{-2}$	48
1	$P(C_6H_5)_3$	145	2.73	0.45	$2.6(3) \times 10^{-3}$	$5.8(7) \times 10^{-3}$	83
2	$P(C_6H_4CH_3)_3$	145	3.84	0.45			
3	$P(C_6H_4OCH_3)_3$	145	4.59	0.45			
4	$P(C_6H_{11})_3$	162	9.70	2.20	$8.4(4) \times 10^{-4}$	$3.8(2) \times 10^{-4}$	570

[a] Data from ref 5. [b] Refers to the ratio of remote isomer **b** to adjacent isomer **a** at equilibrium. [c] Errors were calculated from a least-squares fit at the 95% confidence level.

NMR ($CDCl_3$): (**2a**) δ 7.89 (tt, H_c), 4.36 (d, H_b), 2.30 (m, H_a), −18.90 (d, H_d), J_{aP} 12 Hz, J_{ab} 2 Hz, J_{ac} 13 Hz, J_{bP} 1.5 Hz, J_{bc} 9 Hz, J_{cP} 2 Hz, J_{cd} 1.5 Hz, J_{dP} 7 Hz; (**2b**) δ 8.96 (tt, H_c), 5.30 (d, H_b), 2.50 (dd, H_a), −19.02 (d, H_d), J_{ab} 1.5 Hz, J_{ac} 12 Hz, J_{bc} 10 Hz, J_{cd} 2 Hz, J_{dP} 12 Hz.

(μ-H)$Os_3(CO)_9(P(p\text{-}CH_3OC_6H_4)_3)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$ (3a,b). Anal. Calcd for $C_{32}H_{25}O_{12}Os_3P$: C, 31.95; H, 2.09. Found: C, 32.31; H, 2.27. IR (cyclohexane): ν(CO) 2089 m, 2069 w, 2059 w, 2045 s, 2033 w, 2006 vs, 1985 m, 1968 w, 1957 w cm^{-1}. ^{1}H NMR ($CDCl_3$): (**3a**) δ 7.89 (tt, H_c), 4.35 (d, H_b), 2.28 (m, H_a), −18.92 (d, H_d), J_{ab} 2 Hz, J_{ac} 13 Hz, J_{bP} 1.5 Hz, J_{bc} 9 Hz, J_{cP} 2 Hz, J_{cd} 1.5 Hz, J_{dP} 7 Hz; (**3b**) δ 8.99 (tt, H_c), 5.31 (d, H_b), 2.49 (dd, H_a), −19.02 (d, H_d), J_{ab} 1.5 Hz, J_{ac} 12 Hz, J_{bc} 10 Hz, J_{cd} 2 Hz, J_{dP} 12 Hz.

(μ-H)$Os_3(CO)_9(P(C_6H_{11})_3)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$ (4a,b). Anal. Calcd for $C_{29}H_{37}O_9Os_3P$: C, 30.79; H, 3.30. Found: C, 30.83; H, 3.40. IR (cyclohexane): ν(CO) 2089 w, 2082 m, 2054 s, 2045 s, 2029 s, 2001 vs, 1987 s, 1976 s, 1963 m, 1954 sh, 1941 w cm^{-1}. ^{1}H NMR ($CDCl_3$): (**4a**) δ 7.61 (tt, H_c), 3.89 (d, H_b), 2.35 (m, H_a), −19.51 (d, H_d), J_{ab} 2 Hz, J_{ac} 13 Hz, J_{bP} 1.5 Hz, J_{bc} 10 Hz, J_{cP} 2 Hz, J_{cd} 1.5 Hz, J_{dP} 6 Hz; (**4b**) δ 9.10 (tt, H_c), 5.48 (d, H_b), 2.54 (dd, H_a), −19.71 (d, H_d), J_{ab} 1.5 Hz, J_{ac} 11 Hz, J_{bc} 10 Hz, J_{cd} 2 Hz, J_{dP} 10 Hz.

Preparation of (μ-H)$Os_3(CO)_9(P(C_2H_5)_3)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$ (5a,b). A 300 mL pressure bottle was charged with a solution of (μ-H)$_2Os_3(CO)_9P(C_2H_5)_3$ (21 mg, 0.022 mmol) in *n*-hexane. After the bottle was flushed three times with ethylene, it was pressurized to 40 psig, and the solution was stirred under this atmosphere for 16 h at room temperature. After the bottle was vented, the solvent was removed under reduced pressure, and the residue was purified by thin-layer chromatography, with CH_2Cl_2/*n*-hexane (1:3) as eluent. Red crystals were obtained by recrystallization from pentane (18 mg, 0.018 mmol, 82%). Anal. Calcd for $C_{17}H_{19}O_9Os_3P$: C, 21.07; H, 1.98. Found: C, 20.99; H, 2.17. IR (cyclohexane): ν(CO) 2091 m, 2054 sh, 2045 s, 2029 w, 2008 vs, 2004 vs, 1989 sh, 1978 w, 1966 m, 1951 w cm^{-1}. ^{1}H NMR ($CDCl_3$): (**5a**) δ 7.68 (tt, H_c), 4.18 (dt, H_b), 2.46 (tdd, H_a), −19.88 (d, H_d), J_{ab} 2 Hz, J_{ac} 13 Hz, J_{bP} 1.5 Hz, J_{bc} 10 Hz, J_{cP} 2 Hz, J_{cd} 1.5 Hz, J_{dP} 6 Hz; (**5b**) δ 9.09 (tt, H_c), 4.74 (dt, H_b), 2.62 (m, H_a), −20.08 (d, H_d), J_{ab} 1.5 Hz, J_{ac} 11 Hz, J_{bc} 10 Hz, J_{cd} 2 Hz, J_{dP} 10 Hz.

Preparation of (μ-H)$Os_3(CO)_9(P(CH_3)_3)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$ (6a). A 300 mL pressure bottle was charged with a solution of (μ-H)$_2Os_3(CO)_9P(CH_3)_3$ (35 mg, 0.39 mmol) in *n*-hexane. After the bottle was flushed three times with ethylene, it was pressurized to 40 psig, and the solution was stirred under this atmosphere for 3 h at room temperature. After the bottle was vented, the solvent was removed under reduced pressure, and the residue was purified by thin-layer chromatography, with *n*-hexane as eluent. Red crystals were obtained by recrystallization from pentane (20 mg, 0.021 mmol, 55%). Only isomer **a** could be detected by ^{1}H NMR, which indicates that the equilibrium constant must be less than **b**/**a** = 0.02. Anal. Calcd for $C_{14}H_{13}O_9Os_3P$: C, 18.14; H, 1.41. Found: C, 18.03; H, 1.27. IR (cyclohexane): ν(CO) 2091 m, 2053 sh, 2045 s, 2028 w, 2009 vs, 2004 vs, 1989 sh, 1978 w, 1966 m, 1952 w cm^{-1}. ^{1}H NMR ($CDCl_3$): (**6a**) δ 7.78 (tt, H_c), 4.25 (dt, H_b), 2.55 (tdd, H_a), −19.80 (d, H_d), J_{ab} 2 Hz, J_{ac} 13 Hz, J_{bP} 1.5 Hz, J_{bc} 10 Hz, J_{cP} 2 Hz, J_{cd} 1.5 Hz, J_{dP} 6 Hz.

Kinetic Studies of Interconversion between the Two Vinyl Isomers. Pure isomer **1a** (as judged by ^{1}H NMR) was obtained by preparative-scale thin-layer chromatography (TLC) eluting with 1:3 CH_2Cl_2/*n*-C_5H_{12}. Two narrowly separated bands were observed, and the band with a greater R_f value was extracted from the silica gel with CH_2Cl_2. The solution was quickly evaporated to dryness, and the residue was dissolved in $CDCl_3$. The growth of the hydride ^{1}H NMR signal due to isomer **1b** was followed at 23 °C. Analysis of the data with $K = 0.45$ gave $k_1 = 2.5(3) \times 10^{-3}$ min^{-1} and $k_{-1} = 5.4(7) \times 10^{-3}$ min^{-1}. The errors were calculated from a least-squares line fit to a 95% confidence level. Similiar procedures were used with compounds **2**−**5** except **4a** was obtained by recrystallization from pentane and **5a** was obtained by preparative TLC eluting with pentane.

Preparation of (μ-H)$_2Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)$. Freshly sublimed trimethylamine oxide (1.5 mg, 0.021 mmol) was added to a stirred solution of the vinyl compound (μ-H)$Os_3(CO)_9(PPh_3)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$ (23 mg, 0.021 mmol) in 20 mL of CH_2Cl_2 at room temperature. After 1 h, the solvent was removed under reduced pressure, and the crude product was characterized by its IR (ν(CO)) and ^{1}H NMR spectra,[2] which showed the reaction was quantitative.

NMR Tube Reaction of (μ-H)$Os_3(CO)_9(PPh_3)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$ with Trimethylamine Oxide. Freshly sublimed trimethylamine oxide (10 mg, 0.13 mmol) was dissolved in 2 mL of $CDCl_3$. Successive 50 μL aliquots of the trimethylamine oxide solution were added (every 25 min) to a solution of (μ-H)$Os_3(CO)_9(PPh_3)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$ (10 mg, 0.0090 mmol, in 1 mL of $CDCl_3$) in an NMR tube, and the formation of (μ-H)$_2Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)$ was monitored by ^{1}H NMR spectroscopy. After 1.5 h, the reaction was judged to be complete.

Results and Discussion

Effect of the Phosphine Ligand on the Equilibrium of the Two Vinyl Isomers. The relative amount of the remote isomer **b** at equilibrium varies markedly with the phosphine ligand, ranging from unobservable for L = PMe_3 (<2%) to ca. 70% for L = $P(C_6H_{11})_3$. The data in Table 1 clearly show that the steric bulk of the phosphine ligand determines the equilibrium constant for the two vinyl isomers, whereas the basicity of the phosphine appears to have no influence. The latter point is illustrated by the set of triarylphosphine-substituted compounds (μ-H)$Os_3(CO)_9(P(p\text{-}XC_6H_4)_3)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$, where X = H, CH_3, and OCH_3. The basicity of these three phosphines changes significantly (pK_a = 2.73, 3.84, and 4.59, respectively),[5] but the equilibrium constant is identical for all three vinyl compounds. The set of trialkyl derivatives (μ-H)$Os_3(CO)_9(PR_3)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$ where R = CH_3 (**6a**), C_2H_5 (**5a**,**b**), and C_6H_{11} (**4a**,**b**) dramatically demonstrates the effect of ligand steric bulk on the equilibrium. All of these phosphines are quite basic, but they differ markedly in size. The equilibrium position ranges from having only isomer **a** observable for R = CH_3 to a

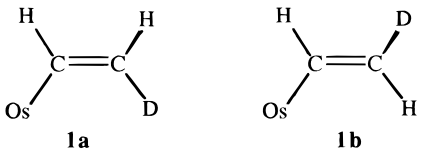
(5) Rahman, M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650.

mixture favoring isomer **a** for R = C_2H_5 to a mixture favoring isomer **b** for R = C_6H_{11}. Taken together, these sets of compounds strongly indicate that in the adjacent isomer the phosphine ligand and the vinyl ligand experience an unfavorable steric interaction, which is relieved by converting to the remote isomer.

Kinetics of the Equilibration of Isomers a and b. We have also studied the effect of different phosphine ligands on the rate of approach to equilibrium for the two vinyl isomers. Table 1 compares these rates for the complexes (μ-H)$Os_3(CO)_9(PR_3)(\mu$-η^2-CH=CH_2) where R = C_2H_5, C_6H_5, and C_6H_{11}. The $t_{1/2}$ values for the three compounds clearly show that the rate is dependent upon the steric bulk of the phosphine used. The cone angles of the phosphines are 132, 145, and 162°,[5] respectively, while the $t_{1/2}$ values are 48, 83, and 570 min. It is significant that the values for k_1 vary only slightly, whereas the values for k_{-1} differ by almost 1 order of magnitude. This indicates that the equilibrium concentration of the two isomers depends primarily on the relative rates of formation of the adjacent isomer from the remote isomer. This result can be interpreted by consideration of the steps in the probable mechanism (vide infra).

Mechanism of the Interconversion of the Two Vinyl Isomers. An important point to consider is that isomer **a** has a *syn*-vinyl orientation, i.e., the α-C−H pointing toward the third osmium center, whereas isomer **b** has an *anti*-vinyl orientation. A stepwise movement of formal σ bonds can suffice to transform *syn*-**a** into *anti*-**b** as mentioned previously.[3] However, detailed analysis shows that there are two possibilities for these steps, and the two possibilities predict different consequences for the configuration of the vinyl ligand. We have therefore undertaken a deuterium-labeling study in order to probe the mechanism of isomerization.

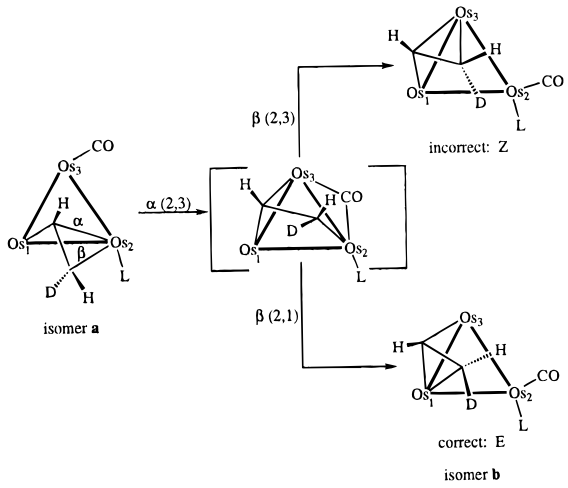
When (μ-D)$_2Os_3(CO)_9(PPh_3)$ is treated with unlabeled acetylene, the two vinyl isomers (**1a**-d_2, **1b**-d_2) with the formula (μ-D)$Os_3(CO)_9(PPh_3)(\mu$-η^2-CH=CHD) result. The ^{1}H NMR spectrum of this sample shows that the deuterium atom on the vinyl ligand is in different locations for each isomer. Specifically, the signal at δ 2.3 due to the hydrogen atom cis to the osmium atom in isomer **1a** and the signal at δ 5.3 due to the hydrogen atom trans to the osmium atom in isomer **1b**, respectively, are missing for the labeled compounds. The basic configurations of the two labeled isomers are shown in the following structures. Isomer **1a**-d_2 has a *Z* configuration, while isomer **1b**-d_2 has an *E* configuration.



1a **1b**

The mechanistic possibilities are summarized in Scheme 2. In all cases, the hydride bridges Os(1) and Os(2), the triphenylphosphine ligand bonds to Os(2), and a carbonyl ligand is transferred from Os(3) to Os(2) during rearrangement. The first step of the isomerization is a shift of the α-C−Os(2) bond to form a new bond between the α-C and Os(3), which would induce a rehybridization of both carbon atoms on the vinyl ligand. There are two routes to re-form the σ,π vinyl species. If

Scheme 2



the β-C−Os(2) bond shifts to form a new bond between the β-C and Os(3) (followed by σ,π vinyl interchange shown to occur in these compounds[3]), the correct vinyl structure would be obtained; however, this mechanism is excluded by the labeling study since this would result in an incorrect *Z* configuration. The correct *E* configuration is obtained if the β-C−Os(2) bond shifts to form a new bond between the β-C and Os(1) instead.

Given the mechanism proposed above, we can now offer an explanation for the steric effects on k_{-1}. Both isomer **a** and the intermediate in the isomerization have five atoms coordinated to the osmium atom with the phosphine ligand; however, the osmium atom with the phosphine ligand has only four atoms in the coordination sphere in isomer **b**. Thus, one would expect the unfavorable steric interactions to be considerably increased in the formation of isomer **a** from isomer **b** and not as much in the formation of isomer **b** from isomer **a**. This would make k_{-1} vary more with the steric bulk of the ligand than k_1, which is consistent with the behavior we have observed in these complexes.

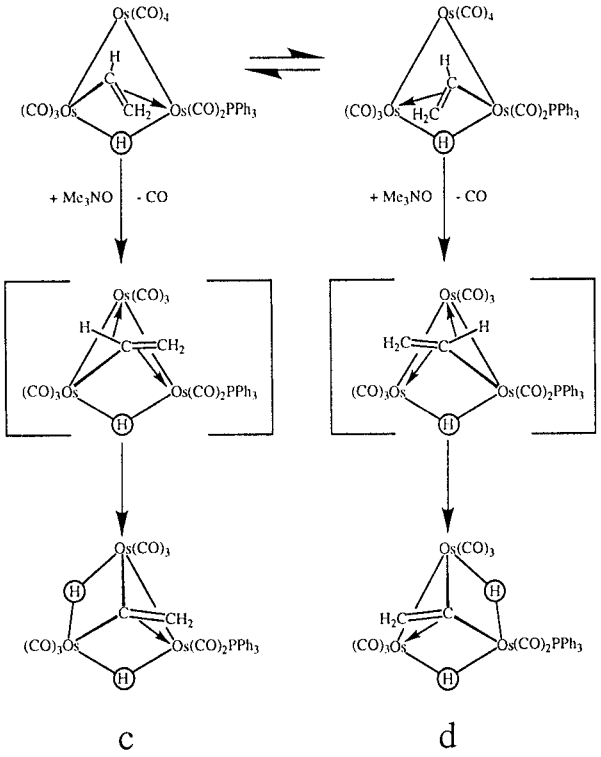
Reaction of (μ-H)$Os_3(CO)_9(PPh_3)(\mu$-η^2-CH=CH_2) with Trimethylamine Oxide. Brown and Evans[2] reported that the thermolysis of (μ-H)$Os_3(CO)_9(PPh_3)(\mu$-η^2-CH=CH_2) yielded the vinylidene compound (μ-H)$_2$-$Os_3(CO)_8(PPh_3)(\mu_3$-η^2-C=CH_2), and ^{1}H and ^{13}C NMR spectral data were used to make the structural assignment c shown in Scheme 3. This conversion is analogous to the thermolysis of the unsubstituted vinyl compound (μ-H)$Os_3(CO)_{10}(\mu$-η^2-CH=CH_2), which produces the vinylidene compound (μ-H)$_2Os_3(CO)_9(\mu_3$-η^2-C=CH_2).[6]

We were intrigued by the fact that only one isomer of the substituted vinylidene compound was formed despite the presence of the two isomers (**1a**,**b**) in the vinyl precursor. Trimethylamine oxide was used to effect the loss of a carbonyl ligand, since this is a gentler method[7,8] and allows the course of the reaction to be monitored more easily. The reaction was quantitative, and only one product was observed (identical to the product reported by Brown and Evans[2]). The reaction

(6) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415.

(7) (a) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem Soc., Dalton Trans.* **1981**, 407. (b) Foulds, G. A.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *296*, 147.

Scheme 3



was repeated in an NMR tube and monitored by ^{1}H NMR spectroscopy. Integration of the hydride signals of the two vinyl isomers showed that the major, adjacent isomer **1a** was consumed faster than the minor, remote isomer **1b** (at one point the ratio of **1a**:**1b** was driven down to 1.4:1 compared to the equilibrium value of 2.2:1).

Scheme 3 shows possible steps in the vinyl to vinylidene conversion. If isomer **1a** were the species that loses a carbonyl ligand, one would expect the product with structure d to be formed. However, structure c could be formed if the σ/π vinyl interchange product of **1a** (previously shown to occur in the compound[3]) were the species that loses a carbonyl ligand. Since both hydride signals for the vinylidene compound show significant coupling to phosphorus, structure c is the likely structure for the compound. The implication is that the vinylidene compound is derived from the σ/π vinyl interchange product of the major isomer (Scheme 3), although rearrangement of ligands on the triosmium moiety cannot be excluded. This is another example of site-selective reactivity in these phosphine-substituted triosmium clusters. In this case, carbonyl loss is inhibited by the presence of the phosphine ligand on the OsL_4 unit. This is most likely the result of greater electron donation to the carbonyl ligand as a result of the greater σ-donating ability of the phosphine, thus preventing attack by trimethylamine oxide. Alternatively, the phosphine ligand might hinder attack of the trimethylamine oxide; however, this seems unlikely, since the thermolysis reaction also gave only a single isomer.[2]

Effect of Phosphine Ligand Steric Bulk on the Reaction of Ethylene with $(\mu\text{-H})_2Os_3(CO)_9(PR_3)$. Also noteworthy is the effect that the steric bulk of the phosphine ligand has on the relative ease of forming a vinyl compound from the reaction of $(\mu\text{-H})_2Os_3(CO)_9(PR_3)$ with ethylene. We have reported that $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)$ requires a moderately high pressure (500 psig) of ethylene to form the **1a**, **1b** mixture,[3] and **4a**, **4b** ($R = C_6H_{11}$) also can only be synthesized by using a comparable pressure of ethylene. In comparison, both the **5a**, **5b** ($R = C_2H_5$) mixture and **6a** ($R = CH_3$) as well as the unsubstituted vinyl compound[9] can be synthesized by using only a modest (ca. 40 psig) pressure of ethylene. Thus, it would appear that increasing the steric bulk of the phosphine ligand inhibits the reaction of the osmium cluster with the entering ethylene moiety. This suggests that the reaction depends on coordination to the osmium atom bearing the phosphine ligand. This finding is consistent with the supposition of Brown and Evans[2] that addition of a nucleophile to the $Os(\mu\text{-H})_2Os$ moiety should occur on the osmium center with the donor substituent, since the LUMO should have greater amplitude at this center. Subsequent steps in the formation of the phosphine ligand substituted vinyl compounds presumably are analogous to those demonstrated for the unsubstituted compound.[10] A probable intermediate, the substituted ethylidene complex $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)(\mu\text{-CHCH}_3)$, has been identified and characterized by ^{1}H and ^{13}C NMR spectroscopic data.[11]

Conclusion. We have illustrated the importance of the steric interactions between a phosphine ligand and a specific hydrocarbon moiety bound as coligands in organotriosmium cluster compounds. Specifically, the steric bulk of the phosphine ligand induces a significant rearrangement of the cluster to compensate for the unfavorable steric interaction between the two ligands. A deuterium-labeling study demonstrates the changes in the stereochemistry of the vinyl ligand that occur during the structural isomerization.

Furthermore, this work provides two examples of site-selective reactivity in phosphine-substituted triosmium compounds. In the reaction of the vinyl cluster $(\mu\text{-H})Os_3(CO)_9(PPh_3)(\mu\text{-}\eta^2\text{-CH=CH}_2)$ with trimethylamine oxide, we have directly observed that loss of a carbonyl ligand is only prevented by the phosphine ligand when it is located on the osmium atom where carbonyl loss occurs. Also, the reaction of $(\mu\text{-H})Os_3(CO)_9(PR_3)$ with ethylene is inhibited when sterically demanding phosphine ligands are utilized, suggesting that the phosphine-substituted osmium atom is the primary reaction site for addition of an alkene.

Acknowledgments. This work was supported by a grant from the National Science Foundation (CHE 94-14217). NMR spectra were obtained using instruments in the Varian Oxford Instrument Center for Excellence in the NMR Laboratory of the School of Chemical Sciences; external funding for this instrumentation was obtained from the Keck Foundation, NIH, and NSF.

OM980015U

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