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# Promotion Effect of Coordinated Isocyanide on the Oxidative Addition of Allyl Bromide in Triosmium Clusters

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The unique linear triosmium clusters $Os_3Br(CO)_{10}(CNR)(\eta^3\text{-}C_3H_5)$ (**2**) are prepared by reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with allyl bromide. The reaction rate is faster in $CH_2Cl_2$ than in cyclohexane. The oxidative addition of allyl bromide to the triosmium cluster is likely to involve a partial heterolytic metal–metal bond fission pathway, and the coordinated isocyanide ligand plays an important role in determining the regioselectivity and the transformation of allyl bromide in the coordination sphere of the cluster. In the absence of the coordinated isocyanide ligand, complex $Os_3(CO)_{11}(NCMe)$ reacts with allyl bromide in $CH_2Cl_2$ to afford a similar linear complex $Os_3Br(CO)_{11}(\eta^3\text{-}C_3H_5)$ (**4**) with a slower rate. Complex $Os_3Br(CO)_{10}(CNPr)(\eta^3\text{-}C_3H_5)$ (**2a**) crystallized in the triclinic space group $P\bar{1}$ with $a = 10.518(5)$ Å, $b = 12.026(2)$ Å, $c = 19.116(3)$ Å, $\alpha = 89.98(1)°$, $\beta = 90.13(3)°$, $\gamma = 93.23(3)°$, $V = 2414(1)$ Å$^3$, $Z = 4$, $R = 4.7\%$, and $R_w = 5.1\%$ for 3810 observed reflections. Both the bromide and the isocyanide ligands coordinate equatorially at the first Os atom, while the allyl group occupies an axial and an equatorial site on the third Os metal center in the linear triosmium cluster.

## Introduction

Mechanistic investigations of ligand addition and substitution reactions at polynuclear metal complexes are of fundamental interest.[1] In addition to the possible dissociative and associative substitutional pathways, polynuclear metal complexes have other available mechanisms including metal–metal bond dissociation without fragmentation and with fragmentation.[2] Many structures having a cleaved metal–metal bond have proposed to explain the intermediates anticipated by the addition of a ligand to high nuclearity clusters.[3,4] A heterolytic metal–metal bond fission mechanism has been proposed by Johnson to account for the kinetic behavior exhibited by a group VIII trinuclear cluster.[3] However, the structure evidence for this mechanism is rare and experimental evidence to support this mechanism is of importance.

In the course of our attempts to get insights into the effect of isocyanide–carbonyl replacement on the reactivity of metal complexes, we have investigated the reactions of $Os_3(CO)_{11}(CNR)$ with amines as well as Brønsted acids.[5] Herein we report the reaction of the "lightly stabilized" complexes $Os_3(CO)_{10}(CNR)(NCMe)$ with allyl bromide. In addition to the isolation of the unique linear triosmium clusters $Os_3Br(CO)_{10}(CNR)(\eta^3\text{-}C_3H_5)$, this reaction exhibits a good comparison to illustrate the role of the coordinated isocyanide ligand on the reactivity of the osmium clusters. The oxidative addition of allyl bromide to a triosmium cluster is likely to involve a partial heterolytic metal–metal bond fission pathway.

## Results

**Reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with Allyl Bromide.** Treatment of the lightly stabilized clusters $Os_3(CO)_{10}(CNR)(NCMe)$ (**1a**, R = Pr; **1b**, R = $CH_2Ph$) with allyl bromide in $CH_2Cl_2$ at room temperature readily gives $Os_3Br(CO)_{10}(CNR)(\eta^3\text{-}C_3H_5)$ (**2a**, R = Pr; **2b**, R = $CH_2Ph$) in good yields with a linear skeleton of triosmium atoms (Scheme 1). The $^1H$ NMR spectrum of **2a** showed five sets of peaks centered at $\delta$ 4.44, 3.64, 2.88, 2.53, and 1.58 assigned to the five protons of the asymmetric allyl group, respectively, which indicates that the C–Br bond of the allyl bromide has been cleaved and the allyl group has been rearranged during the reaction. The heteronuclear $^{13}C$–$^1H$ 2D NMR spectrum (Figure 1) showed that the two protons resonating at $\delta$ 3.63 and $\delta$ 2.53 bind to the carbon atom at $\delta$ 31.09, whereas another set of two protons which

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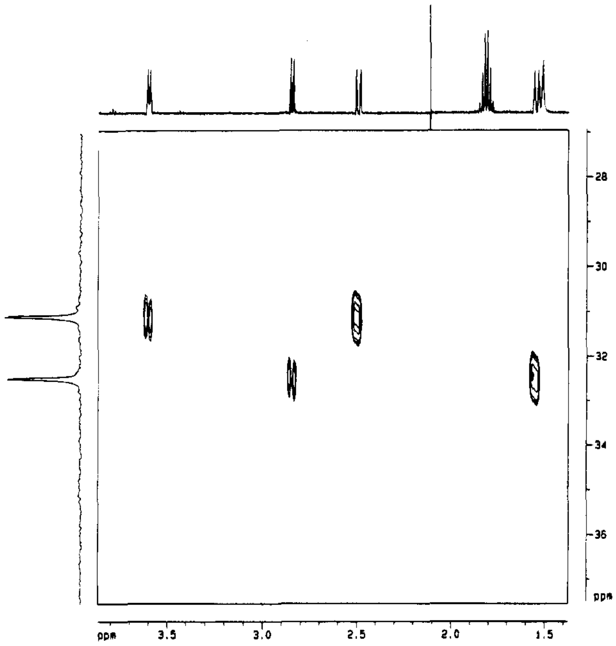
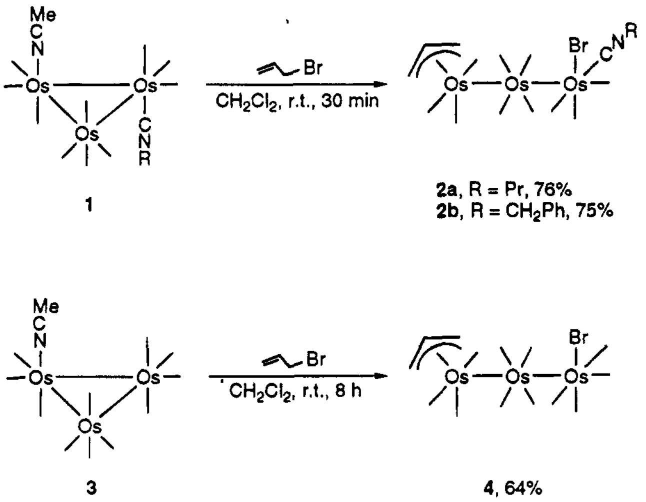


**Figure 1.** Part of the contour plot of the $^1H-^{13}C$ HETCOR spectrum of **2a** recorded at 295 K in $CDCl_3$ solution.

**Scheme 1**



resonate at δ 2.88 and δ 1.58 connect to the carbon atom at δ 32.49 of the allyl group. The IR spectrum of **2a** showed the $\nu_{CN}$ absorption at 2223 $cm^{-1}$, which is characteristic of a terminally coordinated isocyanide ligand.[6] The FAB mass spectrum of **2a** exhibited the molecular ion peak at *m/z* 1044 as well as the subsequent CO-loss fragments.

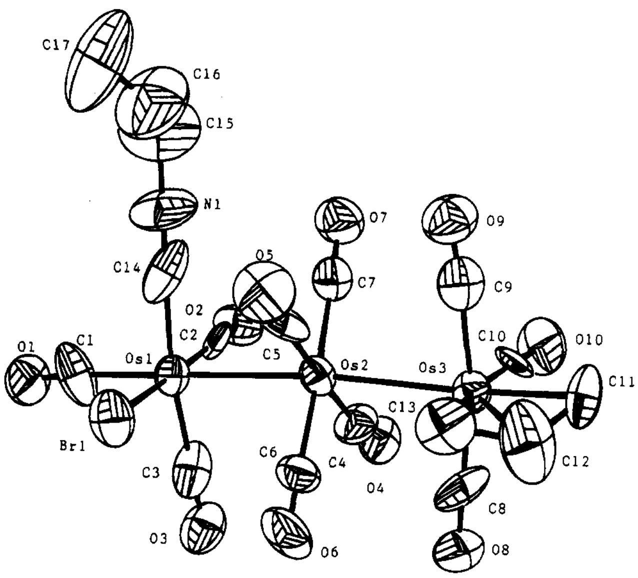


**Figure 2.** ORTEP diagram of $Os_3Br(CO)_{10}(CNPr)(\eta^3-C_3H_5)$ (**2a**).

**Table 1. Crystal and Intensity Collection Data for $Os_3Br(CO)_{10}(CNPr)(\eta^3-C_3H_5)$ (2a)**

| | |
|---|---|
| formula | $C_{17}H_{12}BrNO_{10}Os_3$ |
| fw | 1040.79 |
| space group | $P\bar{1}$ |
| $a$, Å | 10.518(5) |
| $b$, Å | 12.0257(17) |
| $c$, Å | 19.116(3) |
| α, deg | 89.980(13) |
| $\beta$, deg | 90.13(3) |
| $\gamma$, deg | 93.23(3) |
| $V$, Å$^3$ | 2414.1(12) |
| $D_{calc}$, g $cm^{-3}$ | 2.864 |
| $Z$ | 4 |
| μ(Mo Kα), $cm^{-1}$ | 174.6 |
| temp | room temp |
| radiation | Mo Kα |
| $2\theta$ (max) | 44.9 |
| scan type | $\theta/2\theta$ |
| tot. no. of reflcns | 6723 |
| no. of obsd $F_0 > 2.0\sigma(F_o)$ | 3810 |
| no. of obsd variables | 578 |
| $R$ | 0.047 |
| $R_w$ | 0.051 |
| $\Delta(\varrho)$, e Å$^{-3}$ | 1.990 |
| $\Delta/\sigma_{max}$ | 0.274 |
| GOF | 1.98 |

**Crystal Analysis of Structure 2a.** An X-ray structure analysis of **2a** (Figure 2) was undertaken. Pertinent crystallographic data are given in Tables 1–3. The complex crystallized as two crystallographically independent but structurally similar molecules. The three osmium atoms are arranged near linear with ∠Os–Os–Os 174.44(6)°. Both the Br atom and the isocyanide ligand coordinate equatorially at Os(1) and arrange cis to each other. The $\eta^3$-allyl group coordinates at Os(3) with an orientation different from that of the general exo or endo form, as observed in many other ($\eta^3$-allyl)-metal complexes.[7] The carbonyls on any two Os centers are in a staggered arrangement when viewed along an Os–Os bond. A few linear and bent trinuclear osmium clusters without an Os–Os bond between two terminal osmium atoms have been reported in the literature.[8,9] Nevertheless, a linear trisomium cluster containing four

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**Table 2. Atomic Coordinates and Isotropic Thermal Parameters (Å$^2$) for $Os_3Br(CO)_{10}(CNPr)(\eta^3\text{-}C_3H_5)$ (2a)**

| atom | *x* | *y* | *z* | $B_{iso}$[a] |
|---|---|---|---|---|
| Os(1) | 0.30523(11) | 0.11209(9) | 0.34080(6) | 3.96(5) |
| Os(2) | 0.06287(11) | 0.19746(9) | 0.37592(6) | 3.83(5) |
| Os(3) | −0.18360(11) | 0.28698(9) | 0.39681(6) | 4.10(5) |
| Os(4) | 0.06288(11) | 0.69721(9) | 0.12418(6) | 3.83(5) |
| Os(5) | −0.18370(11) | 0.78678(9) | 0.10328(6) | 4.14(5) |
| Os(6) | 0.30521(11) | 0.61199(9) | 0.15921(6) | 4.00(5) |
| Br(1) | 0.3891(3) | 0.3061(3) | 0.2963(2) | 6.3(2) |
| Br(2) | 0.3890(3) | 0.8063(3) | 0.2040(2) | 6.4(2) |
| N(1) | 0.3878(29) | 0.1808(20) | 0.4935(13) | 8.0(16) |
| N(2) | 0.3912(28) | 0.6745(18) | 0.0059(12) | 6.8(15) |
| O(1) | 0.5595(20) | 0.0217(17) | 0.2990(11) | 7.4(12) |
| O(2) | 0.2007(20) | −0.1077(15) | 0.3997(10) | 6.2(11) |
| O(3) | 0.1852(19) | 0.0655(16) | 0.1988(11) | 6.7(12) |
| O(4) | −0.0974(18) | −0.0055(15) | 0.3224(10) | 5.8(10) |
| O(5) | 0.1979(22) | 0.4076(17) | 0.4403(12) | 8.1(13) |
| O(6) | 0.0618(21) | 0.3077(17) | 0.2321(11) | 7.6(12) |
| O(7) | 0.0800(20) | 0.1033(16) | 0.5234(10) | 6.7(11) |
| O(8) | −0.2397(20) | 0.2192(18) | 0.2478(10) | 7.0(12) |
| O(9) | −0.0724(20) | 0.3391(16) | 0.5415(10) | 6.7(11) |
| O(10) | −0.3236(20) | 0.0821(18) | 0.4518(12) | 7.8(13) |
| O(21) | 0.5592(19) | 0.5235(17) | 0.2009(12) | 7.3(13) |
| O(22) | 0.1867(21) | 0.5628(16) | 0.3034(9) | 6.7(11) |
| O(23) | 0.2058(19) | 0.3967(14) | 0.1026(10) | 6.2(11) |
| O(24) | −0.0960(20) | 0.4923(14) | 0.1775(11) | 6.2(11) |
| O(25) | 0.0642(20) | 0.8032(18) | 0.2705(11) | 7.1(12) |
| O(26) | 0.0787(20) | 0.5996(16) | −0.0245(10) | 6.5(12) |
| O(27) | 0.1998(21) | 0.9070(15) | 0.0625(11) | 6.8(12) |
| O(28) | −0.2409(19) | 0.7158(19) | 0.2565(10) | 7.2(13) |
| O(29) | −0.0728(21) | 0.8379(16) | −0.0422(11) | 7.3(12) |
| O(30) | −0.3266(19) | 0.5791(15) | 0.0502(11) | 6.8(11) |
| C(1) | 0.4736(31) | 0.0579(23) | 0.3174(18) | 7.1(18) |
| C(2) | 0.2361(23) | −0.0324(25) | 0.3806(15) | 5.2(16) |
| C(3) | 0.2293(27) | 0.0816(21) | 0.2536(17) | 5.7(17) |
| C(4) | −0.0370(27) | 0.0788(23) | 0.3354(15) | 5.4(15) |
| C(5) | 0.1507(29) | 0.3302(21) | 0.4180(13) | 5.1(15) |
| C(6) | 0.0614(27) | 0.2659(22) | 0.2851(14) | 4.9(15) |
| C(7) | 0.0707(27) | 0.1357(24) | 0.4673(15) | 5.4(16) |
| C(8) | −0.2152(30) | 0.2439(23) | 0.3062(16) | 6.3(17) |
| C(9) | −0.1176(28) | 0.3221(20) | 0.4889(15) | 5.3(16) |
| C(10) | −0.2676(25) | 0.1567(21) | 0.4312(12) | 4.0(13) |
| C(11) | −0.3331(26) | 0.4153(22) | 0.4177(17) | 5.8(17) |
| C(12) | −0.2560(37) | 0.4538(27) | 0.3688(22) | 9.7(24) |
| C(13) | −0.1225(32) | 0.4693(23) | 0.3660(17) | 6.6(18) |
| C(14) | 0.3585(27) | 0.1624(21) | 0.4368(19) | 6.5(19) |
| C(15) | 0.4267(43) | 0.1987(26) | 0.5671(21) | 11.5(28) |
| C(16) | 0.4456(41) | 0.3068(33) | 0.5836(24) | 13.2(29) |
| C(17) | 0.5448(38) | 0.3491(31) | 0.6069(28) | 15.2(33) |
| C(21) | 0.4653(26) | 0.5621(24) | 0.1846(13) | 4.9(15) |
| C(22) | 0.2270(24) | 0.5830(18) | 0.2527(12) | 3.4(12) |
| C(23) | 0.2375(32) | 0.4786(23) | 0.1198(15) | 6.6(18) |
| C(24) | −0.0355(27) | 0.5651(20) | 0.1595(14) | 4.6(14) |
| C(25) | 0.0603(27) | 0.7593(23) | 0.2167(16) | 5.7(16) |
| C(26) | 0.0745(24) | 0.6329(21) | 0.0313(14) | 4.3(13) |
| C(27) | 0.1457(26) | 0.8318(22) | 0.0862(15) | 5.3(15) |
| C(28) | −0.2224(26) | 0.7411(24) | 0.1982(13) | 5.2(15) |
| C(29) | −0.1125(29) | 0.8144(25) | 0.0128(18) | 7.0(18) |
| C(30) | −0.2667(30) | 0.6556(24) | 0.0679(15) | 6.3(17) |
| C(31) | −0.3319(29) | 0.9101(34) | 0.0853(22) | 10.1(25) |
| C(32) | −0.2492(31) | 0.9501(22) | 0.1356(17) | 6.3(17) |
| C(33) | −0.1204(33) | 0.9660(23) | 0.1358(20) | 8.3(22) |
| C(34) | 0.3626(30) | 0.6533(21) | 0.0612(14) | 5.4(16) |
| C(35) | 0.4269(43) | 0.6850(26) | −0.0729(19) | 11.2(26) |
| C(36) | 0.4503(43) | 0.8075(31) | −0.0766(19) | 12.6(27) |
| C(37) | 0.5333(42) | 0.8305(37) | −0.1206(26) | 16.5(33) |

[a] $B_{iso}$ is the mean of the principal axes of the thermal ellipsoid.

**Table 3. Selected Bond Distances and Angles for $Os_3Br(CO)_{10}(CNPr)(\eta^3\text{-}C_3H_5)$ (2a)**

(a) Bond Distances (Å)

| | | | |
|---|---|---|---|
| Os(1)−Os(2) | 2.8820(20) | N(1)−C(14) | 1.14(4) |
| Os(1)−Br(1) | 2.592(3) | N(1)−C(15) | 1.48(5) |
| Os(1)−C(1) | 1.97(3) | O(1)−C(1) | 1.08(3) |
| Os(1)−C(2) | 2.00(3) | O(2)−C(2) | 1.03(3) |
| Os(1)−C(3) | 1.87(3) | O(3)−C(3) | 1.16(4) |
| Os(1)−C(14) | 2.00(3) | O(4)−C(4) | 1.19(3) |
| Os(2)−Os(3) | 2.8912(20) | O(5)−C(5) | 1.11(3) |
| Os(2)−C(4) | 1.89(3) | O(6)−C(6) | 1.13(3) |
| Os(2)−C(5) | 1.97(3) | O(7)−C(7) | 1.15(4) |
| Os(2)−C(6) | 1.92(3) | O(8)−C(8) | 1.18(4) |
| Os(2)−C(7) | 1.90(3) | O(9)−C(9) | 1.13(4) |
| Os(3)−C(8) | 1.83(3) | O(10)−C(10) | 1.12(3) |
| Os(3)−C(9) | 1.93(3) | C(11)−C(12) | 1.31(5) |
| Os(3)−C(10) | 1.874(25) | C(12)−C(13) | 1.41(5) |
| Os(3)−C(11) | 2.30(3) | C(15)−C(16) | 1.34(5) |
| Os(3)−C(12) | 2.25(3) | C(16)−C(17) | 1.22(5) |
| Os(3)−C(13) | 2.33(3) | | |

(b) Bond Angles (deg)

| | | | |
|---|---|---|---|
| Os(2)−Os(1)−Br(1) | 91.13(9) | C(8)−Os(3)−C(9) | 168.8(13) |
| Os(2)−Os(1)−C(1) | 178.3(8) | C(8)−Os(3)−C(10) | 91.5(12) |
| Os(2)−Os(1)−C(2) | 86.2(8) | C(8)−Os(3)−C(11) | 103.6(12) |
| Os(2)−Os(1)−C(3) | 84.4(8) | C(8)−Os(3)−C(12) | 87.9(14) |
| Os(2)−Os(1)−C(14) | 85.1(8) | C(8)−Os(3)−C(13) | 93.6(12) |
| Br(1)−Os(1)−C(1) | 87.5(8) | C(8)−Os(3)−H(12) | 66.6(8) |
| Br(1)−Os(1)−C(2) | 176.2(8) | C(9)−Os(3)−C(10) | 90.5(11) |
| Br(1)−Os(1)−C(3) | 90.2(9) | C(9)−Os(3)−C(11) | 86.8(11) |
| Br(1)−Os(1)−C(14) | 87.4(8) | C(9)−Os(3)−C(12) | 99.0(13) |
| C(1)−Os(1)−C(2) | 95.2(11) | C(9)−Os(3)−C(13) | 87.0(11) |
| C(1)−Os(1)−C(3) | 96.4(13) | C(10)−Os(3)−C(11) | 101.0(10) |
| C(1)−Os(1)−C(14) | 93.9(13) | C(10)−Os(3)−C(12) | 131.4(13) |
| C(2)−Os(1)−C(3) | 92.2(11) | C(10)−Os(3)−C(13) | 165.8(11) |
| C(2)−Os(1)−C(14) | 89.7(11) | C(11)−Os(3)−C(12) | 33.4(12) |
| C(3)−Os(1)−C(14) | 169.2(11) | C(11)−Os(3)−C(13) | 64.9(11) |
| Os(1)−Os(2)−Os(3) | 174.44(6) | C(12)−Os(3)−C(13) | 35.8(13) |
| Os(1)−Os(2)−C(4) | 95.8(9) | C(14)−N(1)−C(15) | 177(3) |
| Os(1)−Os(2)−C(5) | 90.0(8) | Os(1)−C(1)−O(1) | 172(3) |
| Os(1)−Os(2)−C(6) | 88.2(8) | Os(1)−C(2)−O(2) | 178(3) |
| Os(1)−Os(2)−C(7) | 91.1(9) | Os(1)−C(3)−O(3) | 177(3) |
| Os(3)−Os(2)−C(4) | 82.3(9) | Os(2)−C(4)−O(4) | 167.1(25) |
| Os(3)−Os(2)−C(5) | 91.7(8) | Os(2)−C(5)−O(5) | 177(3) |
| Os(3)−Os(2)−C(6) | 86.5(8) | Os(2)−C(6)−O(6) | 178(3) |
| Os(3)−Os(2)−C(7) | 94.3(9) | Os(2)−C(7)−O(7) | 176.2(24) |
| C(4)−Os(2)−C(5) | 173.9(12) | Os(3)−C(8)−O(8) | 177.1(24) |
| C(4)−Os(2)−C(6) | 86.4(12) | Os(3)−C(9)−O(9) | 175.6(24) |
| C(4)−Os(2)−C(7) | 96.6(12) | Os(3)−C(10)−O(10) | 176.2(24) |
| C(5)−Os(2)−C(6) | 92.0(11) | Os(3)−C(11)−C(12) | 71.2(18) |
| C(5)−Os(2)−C(7) | 85.1(11) | Os(3)−C(12)−C(11) | 75.4(19) |
| C(6)−Os(2)−C(7) | 177.0(12) | Os(3)−C(12)−C(13) | 75.1(18) |
| Os(2)−Os(3)−C(8) | 85.1(9) | Os(3)−C(12)−H(12) | 101.9 |
| Os(2)−Os(3)−C(9) | 83.7(8) | C(11)−C(12)−C(13) | 132(4) |
| Os(2)−Os(3)−C(10) | 97.4(8) | Os(3)−C(13)−C(12) | 69.2(17) |
| Os(2)−Os(3)−C(11) | 159.3(7) | Os(1)−C(14)−N(1) | 173.6(24) |
| Os(2)−Os(3)−C(12) | 130.9(10) | N(1)−C(15)−C(16) | 112(3) |
| Os(2)−Os(3)−C(13) | 96.3(8) | C(15)−C(16)−C(17) | 124(4) |

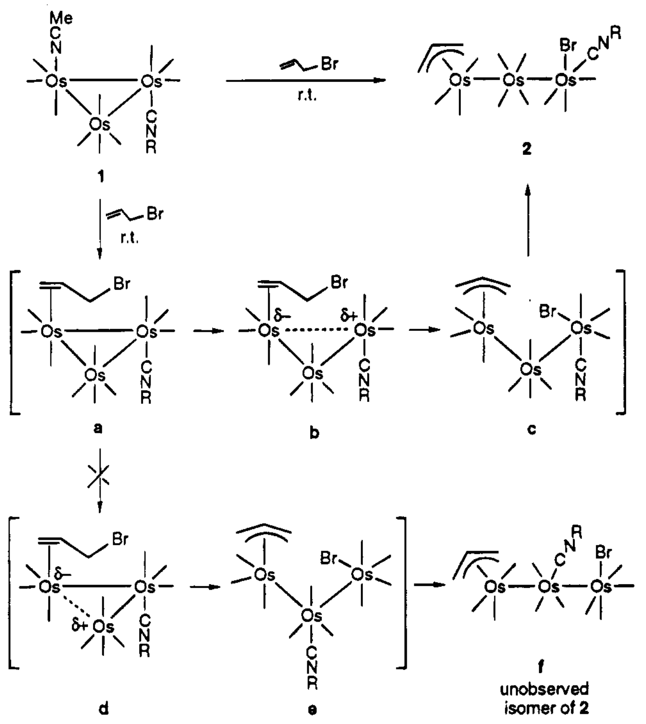
different ligands, i.e., Br, isocyanide, allyl, and carbonyl groups, like complex **2**, is uncommon.

**Reaction of $Os_3(CO)_{11}(NCMe)$ with Allyl Bromide.** A comparison was made to understand the reactivity between $Os_3(CO)_{10}(CNR)(NCMe)$ (**1**) and $Os_3(CO)_{11}(NCMe)$ (**3**) toward allyl bromide. Upon treatment with allyl bromide in $CH_2Cl_2$ at room temperature, we converted $Os_3(CO)_{11}(NCMe)$ to $Os_3Br(CO)_{11}(\eta^3\text{-}C_3H_5)$ (**4**) in 8 h in 64% yield (Scheme 1). The $^1H$ NMR spectrum of **4** showed five sets of peaks centered at $\delta$ 4.54, 3.66, 3.00, 2.56, and 1.70 attributed to the absorption of five hydrogens of the asymmetric allyl group, indicating a structure similar to that of complex **2**.

## Discussion

The reaction of complex **1** with allyl bromide is suggested to proceed initially via the displacement of the labile NCMe ligand and the addition of the C−C double bond of allyl bromide to afford the intermediate $Os_3(CO)_{10}(CNR)(\eta^2\text{-}C_3H_5Br)$ (**a**), as shown in Scheme 2. In this stage, an alternative pathway involving the oxidative addition of C−Br of the allyl bromide to an osmium center is less likely to occur, since no reaction was found to take place between $Os_3(CO)_{10}(CNR)$-

**Scheme 2**



(NCMe) and 1-bromopropane or iodomethane. There are many examples regarding the reaction of $Os_3(CO)_{11}$(NCMe) with less functionalized olefins.[10] Lewis et al. have reported the first monosubstituted $\pi$-bond olefin derivative ($\mu$-H)$Os_3(CO)_{10}(C_2H_4)$.[10a–d] The coordination of olefin at the metal center has been known to be one of the fundamental steps for catalytic olefin hydrogenation in the metal center.[1,2,10f] Poë has proved that the acetonitrile displacement in the $Os_3$ moiety takes place via an initial dissociation of NCMe followed by an associative coordination of the ligand.[1b,4] In the presence of excess acetonitrile, the reaction of **1** with allyl bromide in $CH_2Cl_2$ proceeds with a slower rate compared to the reaction in neat $CH_2Cl_2$, indicating that the behavior of acetonitrile displacement by olefin in complex **1** is in accord with that of Poë's observations.

The introduction of allyl bromide into the Os unit via the coordination of a C—C double bond leads to the formation of intermediate **b** in which the polarization of the Os—Os bond with partial heterolytic bond dissociation is likely to occur.[2,3] The isocyanide ligand displays a stronger $\sigma$-donor and a weaker $\pi$-acceptor character compared to the CO group.[11] A more polar nature of the Os—Os bond is therefore arising, and the partial heterolytic bond dissociation may be expected to occur with greater ease.[3] An $S_N2'$ process with displacement of bromide with the subsequent formation of the $\eta^3$-allyl group is likely to occur, and then the bromide ion attacks the neighboring partially positive charged Os center, leading to the ring opening affording complex **2**. Therefore, both Br and isocyanide ligands coordinate equatorially on the same Os center in **2**. In-situ $^1H$ NMR studies showed that complex **2** was obtained in quantitative yield during the reaction of **1** with allyl bromide. Complex **2** retains its identity, and no evidence shows the existence of the related isomer $(\eta^3\text{-}C_3H_5)Os(CO)_3$—$Os(CO)_3$(CNR)—$OsBr(CO)_4$ (**f**) (Scheme 2) in the course of reaction, chromatography, or crystallization. This indicates that the nucleophilic attack of bromide is likely to occur specifically on the isocyanide coordinated Os center through intermediates **b** and **c** but not **d** and **e** (Scheme 2). The site preference in this reaction is influenced by the coordinated isocyanide ligand which plays a strong role in determining the regioselectivity of the reaction. This kind of site preference for ligand transformation is interesting because metal clusters have been proved to possess low-energy activation pathways leading to reactions with high selectivity in the products.[2] A polar solvent[12] such as $CH_2Cl_2$ or THF promotes the reaction of **1** with allyl bromide more efficiently than the less polar cyclohexane. The reaction is complete within 30 min in $CH_2Cl_2$ or THF; however, more time is needed (2 h) to complete the reaction in cyclohexane. The polar solvent might be able to facilitate the transition state form **b**, and therefore enhance the reaction rate overall.[13]

The linear triosmium clusters $Os_3Br(CO)_{10}(CNR)(\eta^3\text{-}C_3H_5)$ and $Os_3Br(CO)_{11}(\eta^3\text{-}C_3H_5)$ could be seen as stabilized derivatives of the unknown complex $Os_3(CO)_{13}$.[9] Compared to the reactivity of $Os_3(CO)_{11}$(NCMe) (**3**), complex $Os_3(CO)_{10}$(CNR)(NCMe) (**1**) with a coordinated isocyanide group shows a much higher reactivity toward allyl bromide. The coordinated isocyanide group is believed to play an important role in promoting the polarization of the Os—Os bond and inducing a partial Os—Os bond fission pathway during the process of oxidative addition of the allyl bromide to the triosmium cluster.

## Conclusion

In addition to the preparation of the interesting linear triosmium cluster $Os_3(CO)_{10}(CNR)(\eta^3\text{-}C_3H_5)$, this report provides a good example to compare the reactivities of $Os_3(CO)_{11}$(CNR) and $Os_3(CO)_{12}$, showing the influence of isocyanide—carbonyl replacement on the reactivity of the triosmium cluster. The coordinated isocyanide ligand plays an important role in determining the regioselectivity during the oxidative addition and transformation of allyl bromide on the coordination sphere of the triosmium isocyanide cluster and is likely to promote a partial heterolytic Os—Os bond fission pathway.

## Experimental Section

**General Data.** The complexes $Os_3(CO)_{11}$(CNPr) and $Os_3(CO)_{11}(CNCH_2Ph)$ were prepared previously.[5] Other reagents were purchased from commercial sources and were used as received. All manipulations were performed with standard Schlenk techniques. Solvents were dried by stirring over Na/benzophenone (THF) or $CaH_2$ (hexanes, $CH_2Cl_2$, $CH_3CN$) and were freshly distilled prior to use. Infrared spectra were

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(10) (a) Johnson, B. F. G.; Lewis, J.; Pippard, D. *J. Organomet. Chem.* **1978**, *145*, C7. (b) Johnson, B. F. G.; Lewis, J.; Pippard, D. *J. Chem. Soc., Dalton Trans.* **1981**, 407. (c) Johnson, B. F. G.; Lewis, J.; Pippard, D.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1978**, 551. (d) Johnson, B. F. G.; Lewis, J.; Pippard, D. *J. Organomet. Chem.* **1981**, *213*, 249. (e) Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *J. Organomet. Chem.* **1983**, *249*, 149. (f) Atwood, J. D. In *Inorganic and Organometallic Reaction Mechanisms*; Wadsworth, Inc.: Belmont, CA, 1985; pp 203–235.

(11) Lukehart, C. M. In *Fundamental Transition Metal Organometallic Chemistry*; Wadsworth, Inc.: Belmont, CA, 1985; pp 77–78.

(12) Bobbitt, J. M.; Schwarting, A. E.; Gritter, R. J. *Introduction to Chromatography*; Reinhold Book Corp: New York, 1968; p 23.

(13) (a) Gould, E. S. *Mechanism and Structure in Organic Chemistry*; Holt, Rinehart and Winston, Inc.: New York, 1959; p 183. (b) Lu, K. L.; Lo, H.; Lin, Y. C.; Wang, Y. *Inorg. Chem.* **1992**, *31*, 4499.

recorded on a Perkin-Elmer 882 infrared spectrophotometer. NMR spectra were obtained on a Bruker AC-200, an ACP-300, or an AMX-500 FT NMR spectrometer, and mass spectra were recorded on a VG 70-250S mass spectrometer. Elemental analyses were performed by use of a Perkin-Elmer 2400 CHN elemental analyzer.

**Reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with Allyl Bromide.** A solution of $Os_3(CO)_{11}(CNPr)$ (151 mg, 0.16 mmol) in $CH_2Cl_2$ (80 mL) and acetonitrile (2 mL) was treated with a solution of $Me_3NO$ (14 mg, 0.19 mmol) in a mixture of $CH_3CN$ and $CH_2Cl_2$ (1:5, 5 mL). The mixture was stirred for 30 min at room temperature and filtered through a small silica column. The solvent was removed under vacuum, and the residue was redissolved in 50 mL of $CH_2Cl_2$. The resultant solution of $Os_3(CO)_{10}(CNPr)(NCMe)$ was treated with excess allyl bromide (0.1 mL, 1.1 mmol) and stirred for 30 min. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with a mixture of $CH_2Cl_2$ and hexanes (2:3) as eluent to give $Os_3Br(CO)_{10}(CNPr)(\eta^3\text{-}C_3H_5)$ (**2a**, 126 mg, 0.12 mmol) in 76% yield. Treatment of $Os_3(CO)_{10}(CNPr)(NCMe)$ with allyl bromide in THF gave similar results. However, the reaction was slower (2 h) if carried out in cyclohexane. In the presence of excess $CH_3CN$ (0.3 mL), the reaction of $Os_3(CO)_{10}(CNPr)(NCMe)$ (18 mg, 0.02 mmol) with excess allyl bromide (0.06 mL, 0.66 mmol) in $CH_2Cl_2$ (15 mL) was found to complete in 50 min at room temperature. Anal. Calcd for $C_{17}H_{12}BrNO_{10}Os_3$ (**2a**): C, 19.60; H, 1.15. Found: C, 19.62; H, 0.95. IR ($CH_2Cl_2$), $cm^{-1}$: $\nu_{CN}$ 2223 (w); $\nu_{CO}$ 2104 (m), 2069 (s), 2025 (s), 2002 (vs), 1961 (sh). $^1H$ NMR ($CDCl_3$): $\delta$ 4.44 (m, 1 H, CH), 3.98 (t, 2 H, $CNCH_2$), 3.64, 2.88, 2.53, 1.58 (m, 1 $H_a$, 1 $H_b$, 1 $H_c$, 1 $H_d$, respectively, $CH(CH_2)_2$), 1.85 (m, 2 H, $CH_2CH_3$), 1.08 (t, 3 H, $CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 190.09, 185.13, 184.71, 184.16, 179.51, 173.28, 163.65 (CO), 127.78 (CNPr), 86.34 (CH), 47.10 ($CNCH_2$), 32.49 ($CHCH_bH_d$), 31.09 ($CHCH_aH_c$), 22.39 ($CH_2CH_3$), 10.98 ($CH_3$). MS (FAB, $^{191}Os$, $^{81}Br$): *m/z* 1044 ($M^+$), 1016 ($M^+ - CO$), 988 ($M^+ - 2CO$), 960 ($M^+ - 3CO$).

The complex $Os_3Br(CO)_{10}(CNCH_2Ph)(\eta^3\text{-}C_3H_5)$ (**2b**) was obtained under reaction conditions similar to those for **2a** in 75% yield (68 mg, 0.06 mmol) based on $Os_3(CO)_{11}(CNCH_2Ph)$ (83 mg, 0.08 mmol). Anal. Calcd for $C_{21}H_{12}BrNO_{10}Os_3$ (**2b**): C, 23.15; H, 1.10. Found: C, 23.23; H, 1.17. IR ($CH_2Cl_2$), $cm^{-1}$: $\nu_{CN}$ 2220 (w); $\nu_{CO}$ 2104 (m), 2070 (s), 2026 (s), 1998 (vs), 1962 (sh). $^1H$ NMR ($CDCl_3$): $\delta$ 7.38 (m, 5 H, Ph), 5.19 (s, 2 H, $CNCH_2$), 4.42 (m, 1 H, CH), 3.60, 2.80, 2.49, 1.53 (m, 1 H, 1 H, 1 H, 1 H, respectively, $CH(CH_2)_2$).

**Attempted Reaction of $Os_3(CO)_{10}(CNPr)(NCMe)$ with 1-Bromopropane or Iodomethane.** Treatment of $Os_3(CO)_{10}(CNPr)(NCMe)$ with excess 1-bromopropane or iodomethane in $CH_2Cl_2$ at ambient temperature overnight gave no noticeable conversion of the reactants to the expected product.

**Reaction of $Os_3(CO)_{11}(NCMe)$ with Allyl Bromide.** A solution of $Os_3(CO)_{11}(NCMe)$ (90 mg, 0.10 mmol) in $CH_2Cl_2$ (50 mL) was treated with excess allyl bromide (0.1 mL, 1.1 mmol) and stirred for 8 h. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with a mixture of $CH_2Cl_2$ and hexanes (15:85) as eluent to give $Os_3Br(CO)_{11}(\eta^3\text{-}C_3H_5)$ (**4**, 62 mg, 0.06 mmol) in 64% yield. Anal. Calcd for $C_{14}H_5BrO_{11}Os_3$: C, 16.81; H, 0.50. Found: C, 16.74; H, 0.78. IR ($CH_2Cl_2$), $cm^{-1}$: $\nu_{CO}$ 2133 (w), 2088 (m), 2049 (vs), 2018 (vs), 2003 (s), 1988 (sh). $^1H$ NMR ($CDCl_3$): $\delta$ 4.54 (m, 1 H, CH), 3.66, 3.00, 2.56, 1.70 (m, 1 H, 1H, 1 H, 1 H, respectively, $CH(CH_2)_2$). MS (FAB, $^{191}Os$, $^{81}Br$): *m/z* 922 ($M^+ - Br$), 894 ($M^+ - Br - CO$), 866 ($M^+ - Br - 2CO$), 838 ($M^+ - Br - 3CO$).

**Crystallographic Structure Determination.** Crystals of $Os_3Br(CO)_{10}(CNPr)(\eta^3\text{-}C_3H_5)$ (**2a**) were grown from a mixture of $CH_2Cl_2$ and hexanes solutions at $-5$ °C. Specimens of suitable quality were mounted in a thin-walled glass capillary and used for measurement of precise cell constants and intensity data collection. All different measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo K$\alpha$ radiation ($\lambda = 0.709\,30$ Å) with $\theta-2\theta$ scan mode. Unit cells were determined and refined using 25 randomly selected reflections obtained using the CAD-4 automatic search, center, index, and least-squares routines. Anomalous dispersion corrections were applied to all non-hydrogen atoms. Lorentz/polarization (*Lp*) and empirical absorption corrections based on three azimuthal scans were applied to the data for this structure. Compound **2a** crystallized in the triclinic crystal system. The centrosymmetric space group was assumed and later confirmed by the results of refinement. Of 6723 reflections collected ($2\theta < 44.9°$), 6309 were unique, and of these 3810 that were considered observed ($I > 2.0\,\sigma(I)$) were used in the solution and refinement. The structures were solved by the heavy-atom method. All remaining non-hydrogen atoms were located from the difference Fourier map, and they were included in the final refinement cycle and refined by full-matrix least squares. All the data processing was carried out on a Microvax 3600 by use of the NRCC SDP program.[14]

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**Supplementary Material Available:** Tables of atomic coordinates, crystal and intensity collection data, anisotropic thermal parameters, and bond lengths and angles (8 pages). Ordering information is given on any current masthead page.

OM940113P

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[14] Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3*; *Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M.; Krüger, C.; Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 167–174.