The Anomalous Coordination Behavior of Ynamine Ligands in Polynuclear Metal Complexes. The Synthesis and Structural Characterization of $Os_3(CO)_{10}[\mu\text{-}CH_3C_2N(CH_3)_2]$ and $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}H_2CC_2N(CH_3)_2](\mu\text{-}H)$

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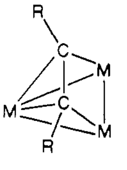
Summary: The ynamine osmium cluster complex $Os_3(CO)_{10}[\mu\text{-}CH_3C_2N(CH_3)_2]$ (**2**) was obtained in 66% yield from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $CH_3C_2N(CH_3)_2$. The ynamine ligand has adopted an unusual edge-bridging coordination mode that has been explained by the existence of strong N–C π bonding between the amino group and the alkyne grouping. Compound **2** was decarbonylated to yield the new cluster complex $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}CH_2C_2N(CH_3)_2](\mu\text{-}H)$ (**3**) in which the ynamine was shifted to the face of the cluster and one of the C–H bonds of the *C*-methyl group was activated.

The activation of alkynes by transition-metal complexes has served as a basis for the development of a wealth of new organic transformations involving these molecules.[1] In trinuclear metal clusters, alkyne ligands have been shown to adopt either of the triply bridging modes A, μ_3-‖, or B, μ_3-⊥.[2] We have recently reported the structural characterization of the complex $Os_3(CO)_9[\mu_3\text{-}HC_2N(C_2H_5)_2](\mu\text{-}H)_2$ (1) which was found to exhibit an anomalous coordination of its "ynamine", $HC_2N(C_2H_5)_2$, ligand.[3] This unusual coordination in 1 was attributed to the existence of a strong bonding interaction between the lone pair of electrons on the nitrogen atom and a π^* orbital of the alkyne ligand.



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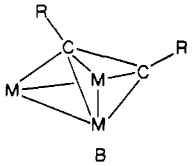

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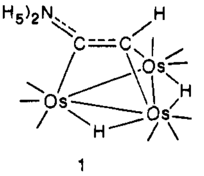

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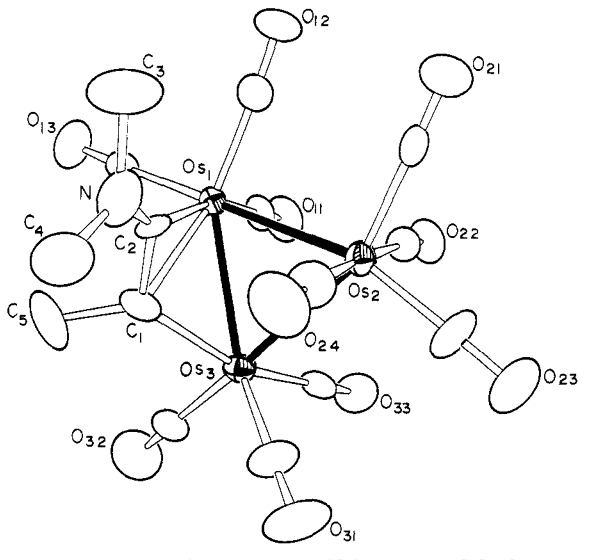

Figure 1. An ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}CH_3C_2N(CH_3)_2]$ (**2**). Selected bond distances (Å) and angles (deg): Os(1)–Os(2) = 2.918 (2), Os(1)–Os(3) = 2.846 (2), Os(2)–Os(3) = 2.871 (2), Os(1)–C(1) = 2.31 (2), Os(1)–C(2) = 2.00 (2), Os(3)–C(1) = 2.07 (2), C(1)–C(2) = 1.42 (3), C(2)–N = 1.38 (3), C(2)–C(1)–C(5) = 112 (2), C(1)–C(2)–N = 128 (2)).

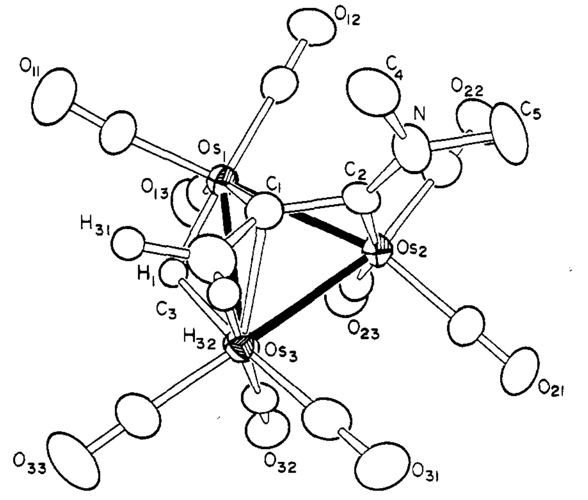

Figure 2. An ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}H_2CC_2N(CH_3)_2](\mu\text{-}H)$ (**3**). Selected bond distances (Å) and angles (deg): Os(1)–Os(2) = 2.8135 (5), Os(1)–Os(3) = 2.8575 (6), Os(1)–C(1) = 2.07 (1), Os(3)–C(1) = 2.272 (9), Os(3)–C(3) = 2.30 (1), Os(2)–C(2) = 2.05 (1), C(1)–C(2) = 1.47 (1), C(1)–C(3) = 1.41 (1), C(2)–N = 1.33 (1), C(3)–C(1)–C(2) = 127 (1), C(1)–C(2)–N = 121.8 (9).

We have now prepared the new ynamine cluster complex $Os_3(CO)_{10}[\mu\text{-}CH_3C_2N(CH_3)_2]$ (**2**) and have found that this ynamine ligand also exhibits an unusual and unexpected coordination mode.[4] An ORTEP drawing of **2** is shown in Figure 1.[5,6] The molecule consists of a triangular cluster of three osmium atoms, ten linear terminal carbonyl ligands, and a $CH_3C_2N(CH_3)_2$ ligand. The ynamine ligand exhibits neither the parallel mode A nor the perpendicular mode B but instead displays an unusual twisted edge-bridging mode.[7] Atom C(1) is coordinated to both Os(1) and Os(3), 2.31 (2) and 2.07 (2) Å, but C(2) is coordinated only to Os(1), 2.00 (2) Å. The C(2)–N bond is short, 1.38 (3) Å, the nitrogen atom is planar, and ^1H NMR spectroscopy shows the presence of a hindered rotation about the C(2)–N bond at reduced temperatures.[4] All of these

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 18. (b) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, pp 649–670.

(2) (a) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

(3) Adams, R. D.; Tanner, J. T. *Organometallics* **1988**, *7*, 2241.

(4) The reaction of $Os_3(CO)_{10}(NCMe)_2$ with $CH_3C{\equiv}CN(CH_3)_2$ in CH_2Cl_2 solvent at 25 °C gave **2** in 66% yield. Orange **2** was isolated by TLC on silica gel. IR (ν(CO), cm^{-1}, in hexane): 2091 m, 2054 s, 2039 vs, 2013 s, 1993 sh, 1988 s, 1975 s, 1969 sh, 1959 w. ^1H NMR (δ in $CDCl_3$): 3.54 (s, 6 H), 2.77 (s, 3 H). The resonance at 3.54 ppm collapses and resolves into two sharp singlets at 3.73 and 3.50 ppm in CD_2Cl_2 at −72 °C; T_c = −46 °C. A satisfactory elemental analysis has been obtained.

(5) Crystals of **2**, grown from hexane/CH_2Cl_2 solutions at 0 °C, belong to the monoclinic crystal system: space group $P2_1$, a = 9.309 (6) Å, b = 11.753 (4) Å, c = 10.056 (5) Å, β = 109.57 (4)°, Z = 2. The structure was solved by direct methods and was refined (2041 reflections) to the final values of the residual, R = 0.035 and R_w = 0.044.

(6) Diffraction data were collected on a Rigaku AFC6 diffractometer by using Mo Kα radiation. Calculations were performed on a MICROVAX II computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., Woodlands, TX. Data were collected for absorption.

(7) A similar ynamine coordination was observed in the diiron complex $Fe_2(CO)_7(\mu\text{-}MeC_2NEt_2)$.[8]

(8) Cabrera, E.; Daran, J. C.; Jeannin, Y.; Kristiansen, O. *J. Organomet. Chem.* **1986**, *310*, 367.

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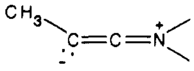
factors are indicative of a significant N–C π-bonding interaction which is believed to supercede and disrupt the metal–alkyne π-back-bonding, and this causes the ligand to shift from the normal triply bridging modes to this unusual edge-bridging mode.[7] The observed coordination can be understood in terms of the heteroallene resonance structure C for the ynamine ligand. A π-coordination of



C

the carbon–carbon double bond to atom Os(1) should produce the bending observed at C(2), C(1)–C(2)–N = 128 (2)°. A σ-donation of the lone pair on carbon C(1) to Os(3) would produce the observed bridging coordination, and the ynamine would then serve as a four-electron donor as required by the EAN rule.

When refluxed in heptane solution for 15 min, compound 2 was decarbonylated and converted to the new compound $Os_3(CO)_9[\mu_3\text{-}H_2CCCN(CH_3)_2](\mu\text{-}H)$ (3) in 90% yield.[9] An ORTEP drawing of 3 is shown in Figure 2.[7,10] The molecule contains a triangular triosmium cluster with nine carbonyl ligands, a triply bridging $H_2CCCN(CH_3)_2$ ligand, and bridging hydride ligand.[11] The latter two ligands were formed by the activation of one of the C–H bonds on the *C*-methyl group of the ynamine ligand and the transfer of the hydrogen atom to the metal atoms. The $H_2CCCN(CH_3)_2$ ligand bridges the face of the cluster through three carbon atoms. As in 2, there is evidence for a strong C(2)–N π-bonding interaction: the nitrogen atom is planar; the C(2)–N distance is short, 1.33 (1) Å, and there is a hindered rotation about the C(2)–N bond that is slow on the ^{1}H NMR time scale even at 100 °C.[12] Mechanistically, the loss of CO from 2 probably occurs at the CO-rich metal atom Os(2). The alkyne ligand might then assume a coordination similar to that in 1 that would bring the *C*-methyl group proximate to the metal atoms Os(1) and Os(3). Formally, this decarbonylated species would be electronically unsaturated, and this should facilitate an intramolecular attack at one of the C–H bonds of the methyl group to form the saturated product 3.[14] Further studies focused on the reactivity of activated ynamine ligand in 2 and 3 are in progress.

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Registry No. 2, 118496-12-1; 3, 94955-83-6; $Os_3(CO)_{10}(NCMe)_2$, 61817-93-4; $CH_3C{\equiv}CN(CH_3)_2$, 7223-38-3; Os, 7440-04-2.

Supplementary Material Available: Tables of crystallographic data, positional parameters, intramolecular distances, intramolecular angles, and anisotropic thermal parameters for compounds 2 and 3 (16 pages); listings of structure factor amplitudes for compounds 2 and 3 (36 pages). Ordering information is given on any current masthead page.

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[9] Yellow 3 was isolated by TLC on silica gel. IR (ν(CO), cm^{-1}, in hexane): 2088 s, 2057 vs, 2035 vs, 2012 s, 2003 s, 1994 s, 1978 s, 1952 m. ^{1}H NMR (δ in CD_2Cl_2): 3.52 (s, 3 H), 3.50 (s, 3 H), 2.10 (br, 2 H), −19.81 (s, br, 1 H). A satisfactory elemental analysis has been obtained.

[10] Crystals of 3, grown from hexane/CH_2Cl_2 solutions at 0 °C, belong to the monoclinic crystal system: space group $P2_1/n$, a = 13.001 (2) Å, b = 10.325 (1) Å, c = 15.570 (2) Å, β = 113.109 (9)°, Z = 4. The structure was solved by direct methods and was refined (3185 reflections) to the final values of the residuals, R = 0.030 and R_w = 0.034.

[11] The hydrogen atoms shown in Figure 2 were located and refined crystallographically.

[12] The ruthenium homologue of 3 is known but was prepared by a different method.[13]

[13] Aime, S.; Osella, D.; Arce, A. J.; Deeming, A. J.; Hursthouse, M. B.; Galas, A. M. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1981.

[14] The 2-butyne complex $Os_3(CO)_{10}(\mu_3\text{-}CH_3C_2CH_3)$ also undergoes activation of a CH bond on one of the methyl groups when it is decarbonylated.[15]

[15] Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.

Carbon Migration along the Fe–Fe Bond during the Transformation of $[(\mu\text{-}\eta^3\text{-}S\overline{CS(CH_2)_2S})Fe_2CO_5L]$ into $[(\mu\text{-}\eta^2\text{-}CH_2{=}CHS\ddot{C}\ddot{S})(\mu\text{-}CH_3S)Fe_2(CO)_5L]$

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Summary: When they are treated with strong bases, cyclic trithiocarbonate complexes of type $[(\mu\text{-}\eta^3\text{-}S\overline{C(1)\text{-}S(CH_2)_2S})Fe_2(CO)_5L]$ (**3a** (L = CO) and **3b** [L = $P(OMe)_3$]) undergo ring opening. After S-alkylation the new complexes $[(\mu\text{-}\eta^3\text{-}SC(1)(SCH{=}CH_2)(\mu\text{-}SCH_3)Fe_2(CO)_5L]$ (**6a** (L = CO) and **6b** [L = $P(OMe)_3$]) are isolated and characterized. The X-ray structure of **6b** proves that this first sequence does not affect the metal coordination spheres. Under thermal activation **6a** and **6b** undergo a C(1)–(SCH_3) cleavage leading ultimately to the carbenic species $[(\mu\text{-}\eta^2\text{-}CH_2{=}CHS\ddot{C}(1)\ddot{S})Fe_2(CO)_5L(\mu\text{-}SCH_3)]$ (**5a** (L = CO) and **5b** [L = $P(OMe)_3$]). During this last step C(1) migrates along the Fe–Fe axis.

Ligand fragmentations and atom migrations in the coordination sphere of polynuclear transition-metal complexes are topics of current interest because unexpected transformations occur under electron-transfer catalysis,[1] under thermal activation,[2] by reaction with strong bases,[3,4] or during ligand exchange processes.[5] We have recently demonstrated that xanthates R–O–C(S)–S–R react with $Fe_2(CO)_9$ affording compounds **1a** which are the precursors of the carbenic complexes **2a**.[6] Under thermal activation

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[1] Lhadi, E. K.; Patin, H.; Darchen, A. *Organometallics* **1984**, *3*, 1128.

[2] Darchen, A.; Lhadi, E. K.; Grandjean, D.; Mousser, A.; Patin, H. *J. Organomet. Chem.* **1988**, *342*, C15.

[3] Seyferth, D.; Womack, G. B.; Cowie, M.; Hames, B. W. *Organometallics* **1983**, *2*, 1696.

[4] Seyferth, D.; Wood, T. G.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1984**, *3*, 1121.

[5] Darchen, A.; Lhadi, E. K.; Patin, H. *J. Organomet. Chem.* **1987**, *327*, C47.