Transformation of an Isocyanide Ligand in the Coordination Sphere of an Osmium Cluster. Reactions of Osmium Isocyanide Complexes with Amines

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Summary: The osmium isocyanide complexes $Os_3(CO)_{11}(CNR)$ (**1**), synthesized from $Os_3(CO)_{12}$ and phosphine imides ($Ph_3P{=}NR$), react with primary amines to afford the carboxamido complexes $Os_3(CO)_{10}(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$ (**2**) with a bridging aminocarbyne. The latter react with excess corresponding amines to yield $Os_3(CO)_9(NH_2R')(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$ (**3**), which when passed through silica gel transform to produce the hydrido complexes $(\mu\text{-}H)Os_3(CO)_9(\mu_2\text{-}CONHR')(CNR)$ (**4**) with the regeneration of the isocyanide ligand. The transformation of the isocyanide ligand with the cleavage and formation of an Os–Os bond may play an important role in mediating the reactivity of the osmium cluster.

Isocyanides are isoelectronic with CO, and the replacement of carbonyl ligands with isocyanides often leads to essentially no change in structural parameters.[1] It is interesting to learn the effect of isocyanide–carbonyl replacement on the reactivity of metal carbonyl complexes. In order to explore the subtle differences in the reactivity between $Os_3(CO)_{12}$ and $Os_3(CO)_{11}(CNR)$, we thus investigated the reaction of osmium isocyanide clusters with nucleophilic reagents. Osmium isocyanide complexes have been less studied due to their relative difficulty of preparation.[2] Phosphine imides, the well-known deoxygenating reagents, readily react with aldehyde or ketone to form Schiff bases.[3] However, to date, there have only been a few examples involving the deoxygenation of carbonyl ligands on metal complexes by phosphine imides.[4,5] We therefore explored this sort of synthetic strategy as an alternative method to the preparation of metal isocyanide complexes. In this communication, we report the preliminary results of the synthesis of the osmium isocyanide cluster $Os_3(CO)_{11}(CNR)$ and the observation of a series of transformations from the reaction of these complexes with amines. The transformation of isocyanide to bridging carbyne, the cleavage and re-formation of an Os–Os bond, and the activation of a carboxamido ligand are the features of these reactions.

$Ph_3P{=}NR$ reacts with $Os_3(CO)_{12}$ in CH_2Cl_2 at room temperature to give the osmium isocyanide complexes $Os_3(CO)_{11}(CNR)$ (**1a**, R = Pr; **1b**, R = Pr^i)[6] in high yields.

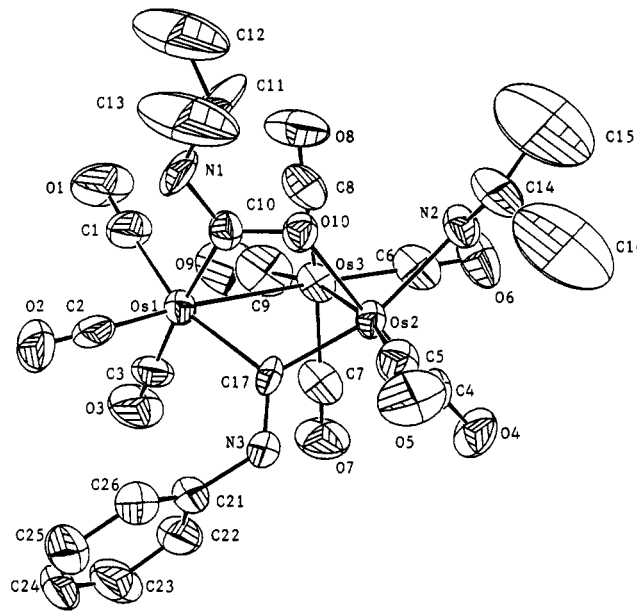

Figure 1. ORTEP diagram of $Os_3(CO)_9(NH_2Pr^i)(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHPh)$ (**3a**).

$Ph_3P{=}NPh$, being a weaker nucleophilic reagent than $Ph_3P{=}NPr$, reacts with $Os_3(CO)_{12}$ in refluxing benzene to form mainly the monoisocyanide complex $Os_3(CO)_{11}(CNPh)$ (**1c**) and the minor diisocyanide complex $Os_3(CO)_{10}(CNPh)_2$. These results show that the ylide type deoxygenation reaction of $Os_3(CO)_{12}$ by phosphine imides can provide an alternative route to the synthesis of osmium isocyanide complexes. In comparison with the method reported earlier by Mays et al.,[2] employing direct replacement of carbonyl ligands on $Os_3(CO)_{12}$ with isocyanide, the present synthetic approach via an ylide type reaction is complementary and has the advantage of proceeding under milder conditions and in high yield.

The osmium isocyanide complexes $Os_3(CO)_{11}(CNR)$ (**1**) react with neat primary amines at room temperature within a few minutes to give the carboxamido complexes $Os_3(CO)_{10}(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$ (**2a–c**)[7] as micro-

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(6) $Os_3(CO)_{11}(CNPr)$ (**1a**): yield 92%. Anal. Calcd for $C_{15}H_7NO_{11}Os_3$: C, 19.01; H, 0.74. Found: C, 19.11; H, 0.72. IR (*n*-hex): ν_{CN} = 2195 (vw), ν_{CO} = 2103 (w), 2056 (s), 2043 (vs), 2025 (m), 2007 (s), 1992 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.98 (t, 2 H, CH_2), 1.76 (m, 2 H, CH_2), 1.04 (t, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 172.0 (br, CO), 173.3 (br, CO), 183.2 (br, CO), 120.9 (CN), 47.1 (CH_2), 22.6 (CH_2), 11.0 (CH_3).

(7) $Os_3(CO)_{10}(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHPh)$ (**2a**): A solution of $Os_3(CO)_{11}(CNPh)$ (150 mg, 0.15 mmol) in NH_2Pr^i (10 mL) was stirred at room temperature for 3 min. The amine was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with hexane as eluent to give **2a** (141 mg, 0.14 mmol, 89%). Anal. Calcd for $C_{21}H_{14}N_2O_{11}Os_3$: C, 24.23; H, 1.36. Found: C, 24.29; H, 1.42. IR (CH_2Cl_2): ν_{CO} = 2091 (w), 2055 (s), 2039 (m), 2004 (s), 1975 (sh), 1960 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.00, 10.85 (br, μ_2-C=N*H*Ph, two isomers in a 5:5 ratio), 7.34–7.43 (m, 5 H, Ph), 5.73 (d, br, 1 H, μ_2-CON*H*Pr^i), 3.96 (m, 1 H, C*H*Me$_2$), 1.04 (d, 6 H, CH_3). $Os_3(CO)_{10}(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHPr)$ (**2b**): yield 91%. IR (CH_2Cl_2): ν_{CO} = 2090 (w), 2053 (s), 2037 (m), 2003 (s), 1975 (sh), 1958 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.16, 9.00 (br, μ_2-C=N*H*Pr, two isomers in a 4:6 ratio), 5.75 (d, br, 1 H, μ_2-CON*H*Pr^i), 3.96 (m, 1 H, C*H*Me$_2$), 3.59 (m, 2 H, $CH_2CH_2CH_3$), 1.87 (m, 2 H, CH_2CH_3), 1.08 (t, 3 H, CH_2CH_3), 1.06 (d, 6 H, $CH(CH_3)_2$). MS (FAB): *m/z* 1009 (M^+), 981 (M^+ – CO), 953 (M^+ – 2CO), 925 (M^+ – 3CO), 897 (M^+ – 4CO), 869 (M^+ – 5CO), 841 (M^+ – 6CO). ^{13}C NMR ($CDCl_3$): δ 272.2, 271.6 (μ_2-CNHPr, 2 isomers), 213.1, 212.9 (μ_2-CONHPr^i, 2 isomers), 186.5, 184.9, 183.0, 182.2, 181.5, 180.4, 180.1, 178.7, 177.4, 177.1, 176.6, 172.9, 172.3, 172.2, 171.5 (CO, 2 isomers), 62.8, 62.6 ($NHCH_2$ and NH*C*H), 42.8 (CH_2CH_3), 22.9, 22.5, 22.3, 21.8 ($CH(CH_3)$), 11.3 (CH_2CH_3).

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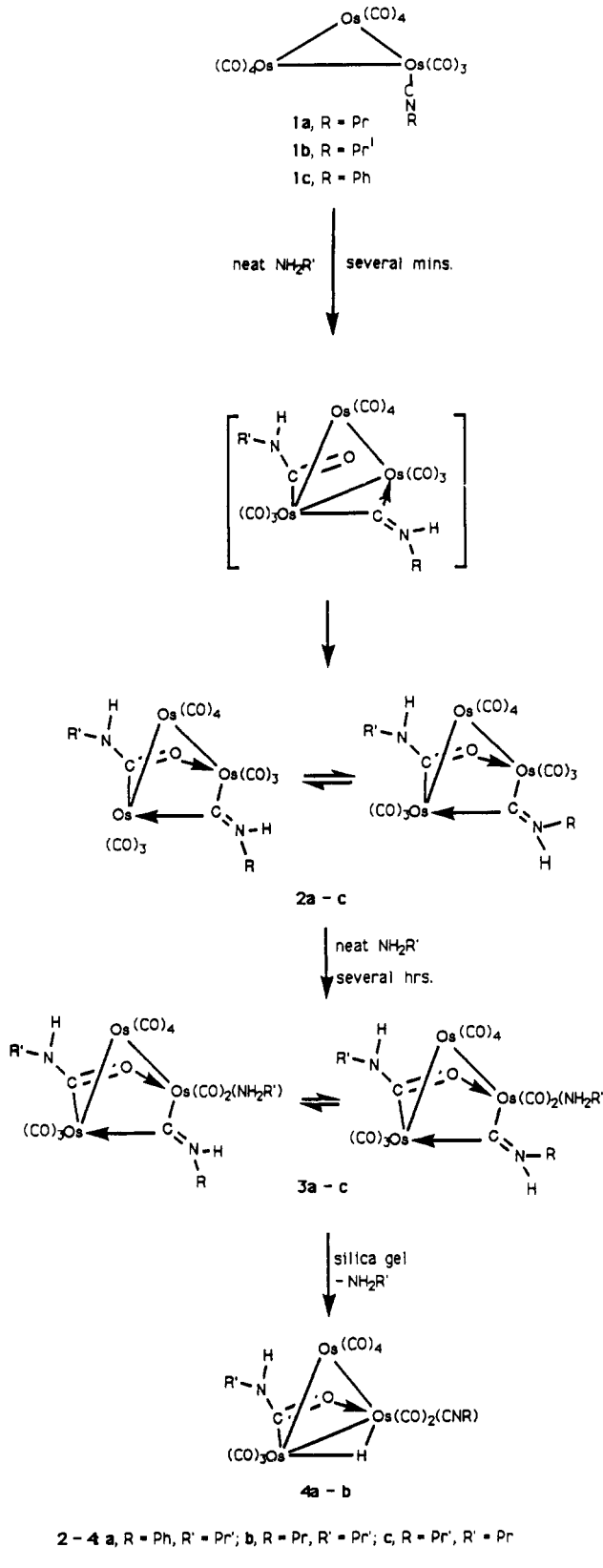
crystalline solids. The rate of reaction of complex **1** with amines decreases in the order Ph > Pr > Pr^i, with the completion time ranging between 3 and 30 min to afford **2**. The more electron withdrawing isocyanide group introduces a more positive charge on the carbonyl carbon, consequently making it more susceptible to nucleophilic attack. Prolonging the reaction for several hours with excess amine gave $Os_3(CO)_9(NH_2R')(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$ (**3a–c**),[8] in which one of the carbonyl ligands is replaced by an amine (Scheme I). All the compounds synthesized were characterized by IR and NMR spectroscopy and mass spectrometry. An X-ray crystal analysis[9] of complex **3a** was also undertaken in order to obtain unambiguous information on its molecular stereochemistry (Figure 1). The molecule is based upon a triangular arrangement of osmium atoms, with Os(1) and Os(2) bridged by both a carboxamido and a aminocarbyne ligand. The doubly bridged Os(1)–Os(2) vector (3.356 (1) Å) is much longer than the nonbridged bonds (Os(2)–Os(3) = 2.9054 (9) Å and Os(1)–Os(3) = 2.9318 (10) Å), indicating that the metal–metal bond has been cleaved. Os(2) is coordinated to an amine and the oxygen of the bridging carboxamido ligand. The ^{1}H NMR spectrum shows that complexes **2** and **3** exist as two isomeric forms (Scheme I) in equilibrium in solution at room temperature. The equilibrium may likely occur due to the restricted rotation about the C–N bond in the bridging carbyne in solution.[10] A high rotational barrier about a C=N bond was also observed by Yin and Deeming[10b] in the related complex $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}C{=}NMeCH_2Ph)$. The ^{1}H NMR spectrum of the isomers of $Os_3(CO)_{10}(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHPr)$ (**2b**) showed two broad singlet peaks at δ 9.16 and 9.00 assigned to the *H*N of the bridging aminocarbyne of each isomer, respectively.

Kaesz and co-workers[11] found that the reaction of amine with $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ proceeds via intermediate η^1-carbamoyl (η^1-C(O)Nu) complexes which transformed to the bridged η^2-carboxamido (μ-O=C(Nu)) complexes as evidenced by spectroscopic data. In our observations, the formation of complex **3** shown in Scheme I has two unique features compared to the previous observations by Kaesz. First, the amine is believed to attack the carbonyl carbon and produce the carbamoyl group (η^1-C(O)Nu) with the transfer of a hydrogen atom from amine to isocyanide to afford the bridging carbyne. Second, the oxygen atom of the carbamoyl ligand attacks the vicinal osmium atom, which leads to the formation of bridged μ-O=C(Nu) derivatives with the concomitant cleavage of the Os–Os bond. It is likely that the complex **2** is stabilized by the bridging carbyne and is isolated as an intermediate which is stable in air.

Scheme I



2 – 4 a, R = Ph, R' = Pr'; **b**, R = Pr, R' = Pr'; **c**, R = Pr', R' = Pr

The facile replacement of CO in the complex $Os_3(CO)_{10}(\mu_2\text{-}OCNHR')(\mu_2\text{-}C{=}NHR)$ (**2**) by amine at ambient temperature indicates some labilization of geminal CO groups cis to the oxygen end of the carboxamido ligand. This is similar to Kaesz's observations[11] and is analogous to the cis-CO-labilizing ability of oxygen donor ligands

(8) $Os_3(CO)_9(NH_2Pr^i)(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHPh)$ (**3a**): A solution of $Os_3(CO)_{11}(CNPh)$ (126 mg, 0.13 mmol) in NH_2Pr^i (10 mL) was stirred at room temperature for 10 h. The amine was removed under vacuum, and the residue was recrystallized from CH_2Cl_2/hexane to give **3a** (114 mg, 0.11 mmol, 83%). Anal. Calcd for $C_{23}H_{23}N_3O_{10}Os_3$: C, 25.76; H, 2.15. Found: C, 25.72; H, 1.90. IR (CH_2Cl_2): ν_{CO} = 2071 (m), 2029 (s), 1992 (s, br), 1982 (s, br), 1958 (sh), 1943 (sh), 1902 (w) cm^{-1} (μ_2-CO = 1436 cm^{-1} (KBr)). ^{1}H NMR ($CDCl_3$): δ 10.63, 10.43 (br, μ_2-C=N*H*Ph, two isomers in a 1:9 ratio), 7.35–7.43 (m, 5 H, Ph), 5.75 (d, br, 1 H, μ_2-CON*H*Pr^i), 4.02 (m, 1 H, μ_2-CONHC*H*Me$_2$), 3.23 (m, 1 H, NH_2CH), 1.27 (dd, 6 H, $NH_2CH(CH_3)_2$), 1.11 (dd, 6 H, μ_2-CONHCH-$(CH_3)_2$).

(9) Crystal data: $P\bar{1}$; a = 8.704 (1), b = 13.100 (2), c = 13.546 (4) Å; α = 93.46 (2), β = 89.91 (2), γ = 106.39 (1)°, V = 1478.9 (5) Å^3, Z = 2, R = 3.8%, R_w = 4.5%. Os(1)–Os(3) = 2.9318 (10), Os(2)–Os(3) = 2.9054 (9), Os(1)–Os(2) = 3.356 (1), Os(1)–C(17) = 2.098 (11), Os(2)–C(17) = 1.991 (13), C(17)–N(3) = 1.339 (18), Os(1)–C(10) = 2.117 (13), Os(2)–O(10) = 2.095 (8), C(10)–O(10) = 1.273 (15), N(1)–C(10) = 1.342 (16), Os(2)–N(2) = 2.233 (12) Å.

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reported in the literature involving metal carbonyls containing phosphine oxides and formate ligands.[12] Further evidence was found in the substitution of acyl complexes as observed by Brown and Bellus.[13] Lin and Lu[14] also observed a similar labilizing effect in their study of the addition of iodine to the metal–metal bond of a (carboxamido)triosmium cluster.

It is interesting that complex **3** is converted into the hydrido complexes (μ-H)$Os_3(CO)_9(\mu_2$-CONHR′)(CNR) (**4a,b**)[15] with the elimination of amine when passed through silica gel. It is most likely that the protonation of **3** by the acidic sites on silica gel, with a consequent elimination of amine, and protonation of the metal–metal bond followed by deprotonation of aminocarbyne lead to the formation of the bridging hydrido complex **4**. Preliminary results obtained when **3** was treated with acetic acid in CH_2Cl_2 at room temperature show that **4** is formed in 50–60% yield. This result is in agreement with the suggestion that the acidic sites on silica may be responsible for the transformation observed. The process of protonation/elimination of amine ultimately creates a vacant site on the Os atom which accommodates the isocyanide ligand. The ^{1}H NMR spectrum of **4a** showed there are three hydride peaks at δ −13.62, −14.24, and −15.06, which may be attributed to the three isomers with different locations of the bridging hydride. The interesting feature of this transformation is that it led to the re-formation of an Os–Os bond which was initially broken. The ready elimination of amine instead of CO during the regeneration of the isocyanide ligand supports the fact that the Os–N bond is weaker than the Os–C bond.

In conclusion, the coordinated isocyanide ligand was observed to mediate the reactivity of the osmium cluster throughout the cluster's reaction with amines. When the isocyanide accepts a hydrogen atom to form the bridging carbyne and the carbamoyl ligand converts to the bridging carboxamido group, the osmium cluster is doubly bridged and cleavage of the Os–Os bond takes place instead of CO elimination. In these reactions the transformations of the coordinated isocyanide, first into the bridging carbyne and then back into the isocyanide with the cleavage and reformation of the Os–Os bond, most likely play an important role in the reactivity of these osmium clusters. Further investigation regardig the labilizing behavior of the O-attacked μ-carboxamido ligand in osmium isocyanide complexes as well as the reactions of these complexes with nucleophilic reagents is in progress.

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Registry No. **1a**, 138957-26-3; **1b**, 138957-27-4; **1c**, 61993-50-8; **2a** (*E* isomer), 138957-28-5; **2a** (*Z* isomer), 138957-29-6; **2b** (*E* isomer), 138957-30-9; **2b** (*Z* isomer), 138957-31-0; **2c** (*E* isomer), 138957-32-1; **2c** (*Z* isomer), 138957-33-2; **3a** (*Z* isomer), 138957-34-3; **3a** (*E* isomer), 138957-34-3; **3b** (*E* isomer), 138957-35-4; **3b** (*Z* isomer), 138957-36-5; **3c** (*E* isomer), 138957-37-6; **3c** (*Z* isomer), 138957-38-7; **4a**, 138957-39-8; **4b**, 138957-40-1; NH_2Pr, 75-31-0.

Supplementary Material Available: A table of analytical and spectroscopic data and tables of atomic coordinates, crystal and intensity collection data, anisotropic thermal parameters, and bond lengths and angles (8 pages); a table of structure factors (13 pages). Ordering information is given on any current masthead page.

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(15) (μ-H)$Os_3(CO)_9(\mu_2$-CONHPr^i)(CNPh) (**4a**): The complex **3a** (100 mg, 0.10 mmol) was chromatographed on a silica gel column with CH_2Cl_2/hexane (10:90) as eluent to afford **4a** (73 mg, 0.07 mmol, 75%). Anal. Calcd for $C_{20}H_{14}N_2O_{10}Os_3$: C, 23.72; H, 1.39. Found: C, 23.62; H, 1.35. IR (*n*-hex): ν_{CN} = 2158 (w), ν_{CO} = 2053 (s), 2033 (s), 1994 (br), 1961 (sh) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.14–7.39 (Ph), 5.56 (d, 1 H, μ_2-CONH), 3.90 (m, 1 H, CHMe$_2$), 0.98 (d, 6 H, CH_3), −15.06, −14.24, −13.62 (s, Os–H–Os, three isomers). MS (EI): *m/z* 1017 (M^+), 988 (M^+ − CO), 960 (M^+ − 2CO), 931 (M^+ − 3CO), 911 (M^+ − CO − Ph), 886 (M^+ − 2CO − Ph).

Synthesis of Bi- and Tetranuclear Sulfur Ylide Complexes of Gold(I) by Phase-Transfer-Catalysis Techniques

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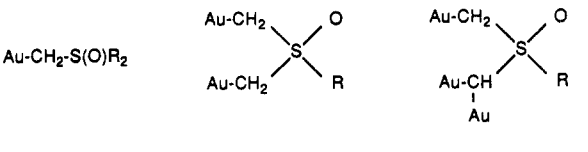
Summary: The luminescent binuclear sulfur ylide gold compound {Au_2(dppm)[$(CH_2)_2$S(O)N($CH_3)_2$]}BF_4 (**1**; dppm = $Ph_2PCH_2PPh_2$) and the tetranuclear sulfur ylide gold compound {Au_4(dppm)($Ph_2PCHPPh_2$)[(μ-CH)(CH_2)S(O)N-$(CH_3)_2$]}BF_4 (**2**) have been synthesized by phase-transfer-catalysis techniques. Crystal structure studies show that the molecules of **1** are packed pairwise with shorter inter- than intramolecular Au···Au distances and that **2** has triply bridging $Ph_2PCHPPh_2^-$ and (CH)(CH_2)S(O)N-$(CH_3)_2^{2-}$ ligands.

In contrast to the analogous phosphorus ylide complexes,[1] sulfur ylide complexes of gold are rare.[2] In the known gold complexes,[2] sulfur ylide coordinated as a terminal ligand (type A). To our knowledge, a gold complex with a type B or C bonding mode has never been reported. Type C bonding is not even known for other



A B C

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