Regioselective addition of an alkyne to both CO and CNPr functionalities in osmium clusters

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Reaction of $[Os_3(CO)_{10}(CNPr)(NCMe)]$ with methyl propiolate at 0 °C gave $[Os_2(CO)_6\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}C(OH)C(CO_2Me)=CHCNHPr\}]$ as the major product and $[Os_2(CO)_6\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}C(OH)CH=C(CO_2Me)CNHPr\}]$ as the minor product, in which two kinds of C–C bond formations occur regioselectively involving coupling of alkyne and CO as well as coupling of alkyne and CNPr; the stereochemistry is likely to be mediated by the co-ordinated isocyanide.

The investigation of carbon–carbon bond formation has attracted considerable attention in view of its relevance to catalysis and organic synthesis.[1] Transition-metal complexes play an indispensable role in this process. It has been observed that alkynes may couple with other alkynes, with CO, or with isocyanides to form metal–alkylidene bonds.[2–4] However, little is known about the C–C coupling reactions of alkynes with both CO and CNR simultaneously mediated by metal centres. In the course of our attempts to evaluate the influence of isocyanide–carbonyl replacement on the reactivity of metal complexes we have previously reported several cases involving unusual C–H activation and C–C coupling reactions in triosmium complexes.[5] Here we describe an unprecedented regioselective addition of alkyne with both CO and CNPr groups in osmium clusters. The co-ordinated isocyanide may play an important role in determining the regioselectivity for the insertion of unsymmetrical alkyne.

The complex $[Os_3(CO)_{10}(CNPr)(NCMe)]$ **1** reacts readily with an excess of methyl propiolate in CH_2Cl_2 at 0 °C for 10 min to give the major product $[Os_2(CO)_6\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}$

$C(OH)C(CO_2Me)=CHCNHPr\}]$ **2** in 37% yield and the minor complex $[Os_2(CO)_6\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}C(OH)CH=C(CO_2Me)CNHPr\}]$ **3** in 7% yield (Scheme 1).† The ^1H NMR spectrum of **2** showed a singlet at δ 11.08 corresponding to the resonance of the HN of the co-ordinated $\mu\text{-}\eta^2\text{:}\eta^3\text{-}C(OH)C(CO_2Me_2)=CHCN H Pr$ group, whereas the peaks of HC and HO of the ligand overlapped and appeared at δ 5.12. After D_2O exchange the HN signal at δ 11.08 disappeared, and the peak at δ 5.12 decreased its intensity to an integration area of one hydrogen atom, indicating disappearance of the HO signal. The HC peak was further confirmed by the heteronuclear ^1H–^{13}C (HMQC) spectrum of **2**, which showed the proton resonating at δ 5.12 binds to a carbon atom at δ 47.8. The FAB mass spectrum of **2** exhibited the molecular ion peak at m/z 735 and peaks corresponding to subsequent CO-loss fragments. The ^1H NMR spectrum of **3** showed three singlets at δ 9.94, 6.55 and 5.42 assigned to the resonances of HN, HC and HO, respectively. The FAB mass spectrum of **3** with a molecular ion at m/z 735 confirmed that complexes **2** and **3** are isomers. Their formation involves the fragmentation of the triosmium cluster. In addition a complex mixture was also observed during the reaction. The third Os atom is suggested to be involved in these by-products. Attempts to characterize the reaction intermediates by spectroscopic means were unsuccessful. The co-ordinated isocyanide in **1** underwent two kinds of interactions including a C–C bond formation with the alkyne and protonation of the nitrogen atom. The proton source is likely to be impurities in the reagent and not CH_2Cl_2 as the same products were obtained when CD_2Cl_2 was used as solvent.

In addition to spectroscopic studies, the structure of complex **2** was further defined by X-ray diffraction analysis.‡ An ORTEP[7] drawing is given in Fig. 1. The two osmium atoms separated by 2.8132(7) Å are asymmetrically bridged by a

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† A solution of $[Os_3(CO)_{11}(CNPr)]$ (120 mg, 0.127 mmol) in CH_2Cl_2 (50 cm³) and MeCN (1 cm³) was treated with a solution of Me_3NO (15 mg, 0.200 mmol) in CH_2Cl_2 (5 cm³) to form $[Os_3(CO)_{10}(CNPr)(NCMe)]$. The latter was treated with an excess of methyl propiolate (150 μl, 1.69 mmol) in CH_2Cl_2 (70 cm³) at 0 °C for 10 min. The solvent was then removed under reduced pressure and the residue purified on a silica gel TLC plate with CH_2Cl_2 as the eluent to afford $[Os_2(CO)_6\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}C(OH)C(CO_2Me)=CHCNHPr\}]$ **2** (35 mg, 0.046 mmol, 37%) and $[Os_2(CO)_6\{\mu\text{-}\eta^2\text{:}\eta^3\text{-}C(OH)CH=C(CO_2Me)CNHPr\}]$ **3** (7 mg, 0.009 mmol, 7%). Complex **2** (Found: C, 24.7; H, 1.85; N, 1.65. Calc. for $C_{15}H_{12}NO_9Os_2$: C, 24.65; H, 1.65; N, 1.9%): IR (CH_2Cl_2) ν(CO) 2076w, 2043vs, 1998s and 1973m cm⁻¹; ^1H NMR $(CDCl_3)$ δ 11.08 (s, 1 H, NH), 5.12 (s, br, 2 H, CH and OH), 3.87 (s, 3 H, OCH_3), 3.17 (m, 1 H, $CH_aCH_bCH_2CH_3$), 3.05 (m, 1 H, $CH_aCH_bCH_2CH_3$), 1.56 (m, 2 H, $CH_2CH_2CH_3$) and 0.94 (t, 3 H, $J = 7.6$ Hz, $CH_2CH_2CH_3$); mass spectrum (FAB, ^{192}Os) m/z 735 (M^+), 707 ($M^+ - CO$), 679 ($M^+ - 2CO$), 651 ($M^+ - 3CO$), 623 ($M^+ - 4CO$), 595 ($M^+ - 5CO$) and 567 ($M^+ - 6CO$). Complex **3**: IR (CH_2Cl_2) ν(CO) 2074w, 2041vs, 1998s and 1967m cm⁻¹; ^1H NMR $(CDCl_3)$ δ 9.94 (s, 1 H, NH), 6.55 (s, 1 H, CH), 5.42 (s, 1 H, OH), 3.75 (s, 3 H, OCH_3), 3.36 (m, 1 H, $CH_aCH_bCH_2CH_3$), 3.28 (m, 1 H, $CH_aCH_bCH_2CH_3$), 1.62 (m, 2 H, $CH_2CH_2CH_3$) and 0.97 (t, 3 H, $J = 7.4$ Hz, $CH_2CH_2CH_3$); mass spectrum (FAB, ^{192}Os) m/z 735 (M^+), 707 ($M^+ - CO$), 679 ($M^+ - 2CO$), 651 ($M^+ - 3CO$), 623 ($M^+ - 4CO$) and 595 ($M^+ - 5CO$).

‡ $C_{15}H_{13}NO_9Os_2$ **2**, $M = 731.66$, monoclinic, space group $P2_1/n$, $a = 9.148(2)$, $b = 17.514(2)$, $c = 12.215(2)°$, β = 101.01(2)°, $U = 1921.0(6)$ Å³, $Z = 4$, $D_c = 2.530$ g cm⁻³, crystal dimensions $0.25 \times 0.25 \times 0.25$ mm, $F(000) = 1336$. λ = 0.710 69 Å, μ(Mo-Kα) = 13.262 mnm⁻¹. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer by the ω–2θ method ($2\theta_{max} = 45°$); of 2672 reflections measured, 1966 were considered observed $[I > 2\sigma(I)]$. The structure was solved by direct methods and refined by full-matrix least squares using NRCVAX.[6] All non-hydrogen atoms were anisotropically refined. $R = 0.0336$, $wR(F^2) = 0.0903$. $C_{15}H_{13}NO_9Os_2$ **3**, $M = 731.66$, triclinic, space group $P\bar{1}$, $a = 9.4455(5)$, $b = 12.7473(14)$, $c = 17.082(2)$ Å, α = 86.173(10), β = 85.739(10), γ = 73.053(10)°, $U = 1959.8(3)$ Å³, $Z = 4$, $D_c = 2.480$ g cm⁻³, crystal dimensions $0.25 \times 0.13 \times 0.19$ mm, $F(000) = 1336$, μ(Mo-Kα) = 13.000 mm⁻¹. Intensity data were collected as for complex **2**; of 5496 reflections measured, 3445 were considered observed $[I > 2\sigma(I)]$. The structure was solved and refined as for **2**: $R = 0.0286$, $wR(F^2) = 0.0728$. The two independent formula units in the asymmetric unit are pseudo-symmetrically related. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/321.
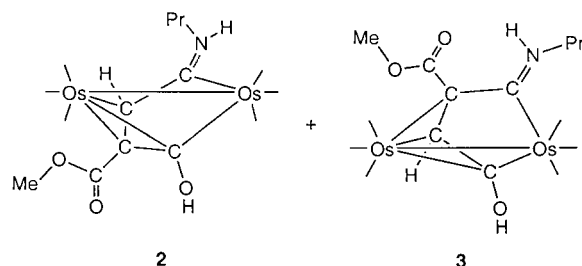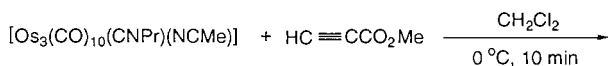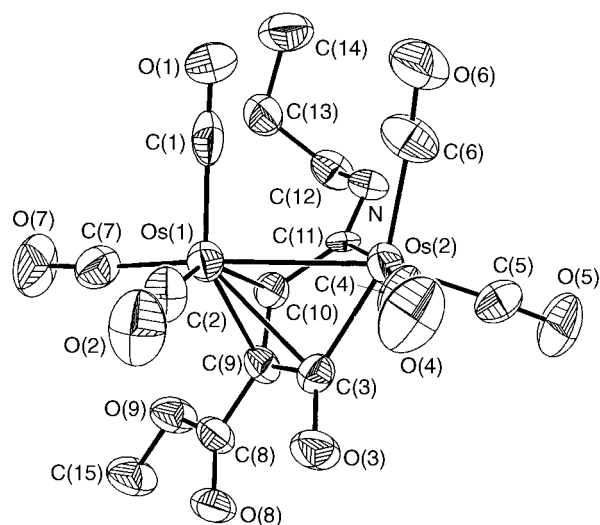
Scheme 1

Fig. 1 An ORTEP diagram of complex **2**. Selected bond distances (Å): Os(1)–Os(2) 2.8132(7), Os(2)–C(3) 2.04(1), C(3)–C(9) 1.44(2), C(9)–C(10) 1.43(2), C(10)–C(11) 1.45(2), C(11)–N 1.34(1), C(3)–O(3) 1.35(1), Os(1)–C(9) 2.18(1), Os(1)–C(10) 2.21(1) and C(8)–O(8) 1.21(1)

μ-η^2:η^3-C(OH)C(CO$_2$Me)=CHCNHPr group. The methyl propiolate ligand couples with both a CO ligand and the isocyanide group. The bond distances of C(9)–C(3) [1.44(2) Å] and C(9)–C(10) [1.43(2) Å] in the allyl group show partial double-bond character similar to that found in the related complex [(η-C$_5$Me$_5$)(OC)$_2$Re{μ-η^1:η^3-CH=C(CMe=CH$_2$)CO}Re(CO)(η-C$_5$-Me$_5$)].[8] Furthermore, C(3)–O(3), C(10)–C(11) and C(11)–N also show partial double-bond character,[9] suggesting π delocalization throughout the five bonds O(3)–C(3)–C(9)–C(10)–C(11)–N.

An X-ray analysis of complex **3** was also undertaken (Fig. 2).‡ The molecule consists of a dinuclear complex with a distance Os(1)–Os(2) of 2.7905(7) Å. The Os atoms are bridged by a μ-η^2:η^3-C(OH)CH=C(CO$_2$Me)CNHPr group, in which the chain O(7)–C(7)–C(8)–C(9)–C(12)–N possesses five partial-double bonds, indicating that π delocalization also exists over these bonds.

Examination of the crystal structures of complexes **2** and **3** illustrates that regioselective couplings of the alkyne with both CO and CNR during the reaction of [Os$_3$(CO)$_{10}$(CN-Pr)(NCMe)] and methyl propiolate. Two kinds of C–C bond formations including coupling of alkyne and CO as well as coupling of alkyne and CNPr are observed here.[10,11] To our knowledge this is the first demonstration of an alkyne molecule coupling with CO and CNR simultaneously in a metal cluster.
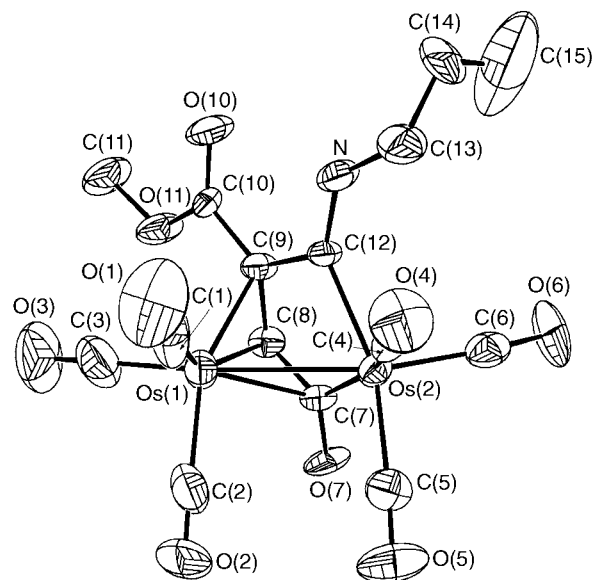

Fig. 2 An ORTEP diagram of complex **3**. Selected bond distances (Å): Os(1)–Os(2) 2.7905(7), Os(2)–C(7) 2.08(1), C(7)–C(8) 1.35(1), C(8)–C(9) 1.45(1), C(9)–C(12) 1.44(1), C(12)–N 1.32(1), C(7)–O(7) 1.35(1), Os(1)–C(7) 2.38(1), Os(1)–C(8) 2.175(9), Os(1)–C(9) 2.21(1) and C(10)–O(10) 1.22(1)

The steric effect of the isocyanide ligand is most likely to control the regioselective addition of the alkyne, leading to the formation of two isomers, **2** and **3**, in a ratio of 5:1. The co-ordinated μ-η^2:η^3-allylidene groups in **2** and **3**, are rare in dinuclear metal complexes or metal clusters.[8,10]

Acknowledgements

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