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200 instrument at $T^\circ = 298$ K. The standard PENMR method, including a rotation frequency of the sample of 2500 Hz, was used. The contact time introduced was 5 ms.

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Supplementary Material Available: Full tables of data collection parameters, atomic fractional parameters, hydrogen fractional parameters, anisotropic thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

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Synthesis of $Os_3(CO)_{10}(CNR)(NCMe)$ and Its Reaction with Propynoic Acid

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The nitrile derivatives $Os_3(CO)_{10}(CNR)(NCMe)$ (2) have been prepared by the reaction of isocyanide complexes $Os_3(CO)_{11}(CNR)$ (1) with Me_3NO in the presence of CH_3CN. The labile complex 2 on reaction with two-electron donor ligands L (L = CO, PPh_3, $PMePh_2$) gives $Os_3(CO)_{10}(CNR)L$ (3). Treatment of 2 with propynoic acid ($HC{\equiv}CCO_2H$) in CH_2Cl_2 yields the hydrido complexes $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(CNR)$ (4); however, complex 2 reacts with propynoic acid in acetonitrile to form complex 4 and the bridging aminocarbyne species $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHR)$ (5) containing a unique bridging unidentate (μ_2-η^1-oxo) carboxylate ligand. Molecular structures of $Os_3(CO)_{10}(CNPr)(PPh_3)$ (**3a**) and $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHPr)$ (**5a**) have been determined by X-ray diffraction studies. Crystal data are as follows. **3a**: $P\bar{1}$; $a = 11.4611$ (14), $b = 11.6963$ (19), $c = 14.9661$ (22) Å; $\alpha = 93.635$ (12), $\beta = 73.633$ (11), $\gamma = 117.325$ (11)°; $V = 1705.0$ (4) Å^3, $Z = 2$; $R = 4.2\%$, $R_w = 5.1\%$. **5a**: $P2_12_12_1$; $a = 9.4241$ (23), $b = 15.414$ (4), $c = 15.972$ (3) Å; $V = 2320.2$ (9) Å^3, $Z = 4$; $R = 3.2\%$, $R_w = 3.5\%$.

Introduction

Isocyanides are known to be isoelectronic with CO,[1] and it is of interest to learn the effect of replacement of carbonyl ligands with isocyanide on the reactivity of metal carbonyl complexes. Although the coordinated isocyanide has been demonstrated to be capable of reacting with a hydrogen atom to form a bridging formimidoyl or a bridging aminocarbyne ligand in the osmium cluster sphere,[2] this aspect of chemistry has not been extensively studied probably due to the relatively difficult preparation of the osmium isocyanide cluster. Recently we have reported a high-yield route to the synthesis of the osmium isocyanide clusters $Os_3(CO)_{11}(CNR)$ by the reaction of $Os_3(CO)_{12}$ with phosphine imides.[3] Considering the importance of oxy ligands of various sorts in the chemical modification of CO in a cluster or on a surface,[4,5] we therefore started to study the interactions of the osmium isocyanide complexes with Brønsted acids in order to examine the transformation or coordination behavior of the oxy and isocyanide ligands in trinuclear osmium clusters. In this paper, we report the preparation of the labile nitrile complexes $Os_3(CO)_{10}(CNR)(NCMe)$ and their reactions with propynoic acid. The features of these reactions are the transformation of the isocyanide ligand and the unique bridging unidentate coordination mode (μ_2-η^1-O) of the carboxylate ligand in the cluster sphere.

Results and Discussion

Preparation of Acetonitrile Complexes $Os_3(CO)_{10}$(CNR)(NCMe). Treatment of the osmium isocyanide complexes $Os_3(CO)_{11}(CNR)$ (1) in CH_2Cl_2 with Me_3NO in the presence of CH_3CN at room temperature yields the acetonitrile complexes $Os_3(CO)_{10}(CNR)(NCMe)$ (**2a**, R = Pr; **2b**, R = Pr^i; **2c**, R = Ph) in good yield (eq 1). The

$$\underset{1}{Os_3(CO)_{11}(CNR)} \xrightarrow[\text{CH}_2\text{Cl}_2 \atop \text{r.t.}]{\text{Me}_3\text{NO / CH}_3\text{CN}} Os_3(CO)_{10}(CNR)(NCMe) \qquad (1)$$

2a, R = Pr, 78%
2b, R = Pr^i, 76%
2c, R = Ph, 81%

reactions were monitored by IR spectroscopy by following the disappearance of ν_{CO} bands of the starting material, $Os_3(CO)_{11}(CNR)$. In general, slightly more than a stoichiometric amount of Me_3NO was required. The yellow complexes $Os_3(CO)_{10}(CNR)(NCMe)$ are "lightly stabilized" in CH_2Cl_2 solution and decompose slowly to light green materials, but they are stable in the presence of acetonitrile and can be recrystallized from a mixture of hexane/CH_2Cl_2/CH_3CN. The infrared spectrum of **2c** shows the $\nu_{C\equiv N}$ absorption at 2160 cm^{-1}, which is characteristic of terminally coordinated isocyanide ligand.[2] The FAB mass spectrum of **2c** shows the molecular ion at m/z 997 as well as the subsequent CO-lost fragments. In addition to the appropriate isocyanide ligand ^{1}H NMR resonance, each derivative displays one intense signal for the methyl group of acetonitrile ligand near δ 2.65. No evidence was found for the formation of diacetonitrile derivatives $Os_3(CO)_9(CNR)(NCMe)_2$ in CH_2Cl_2 even in the presence of a de-

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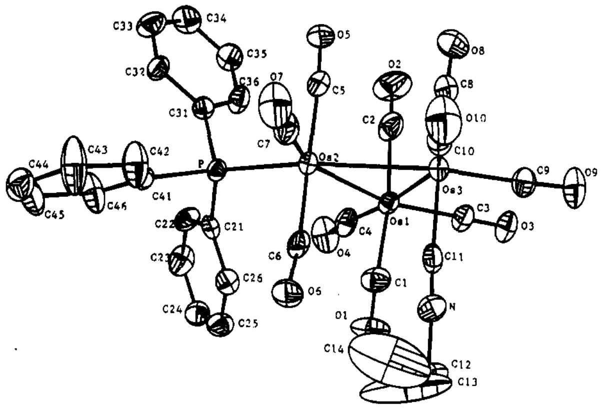


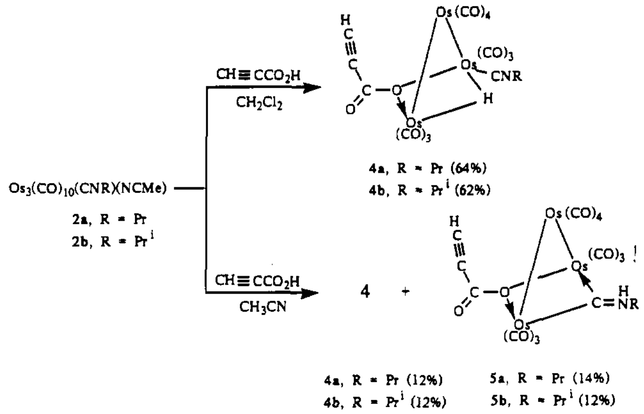
Figure 1. ORTEP diagram of $Os_3(CO)_{10}(CNPr)(PPh_3)$ (**3a**).

carbonylating reagent, Me_3NO.

Reactivity of $Os_3(CO)_{10}(CNR)(NCMe)$. The reactivity of the nitrile complexes $Os_3(CO)_{10}(CNR)(NCMe)$ was primarily examined by interacting with two-electron donor ligands. Bubbling CO gas through a solution of complex **2** in CH_2Cl_2 gives $Os_3(CO)_{11}(CNR)$ (**1**) in almost quantitative yield, when monitored with IR spectroscopy. Addition of PPh_3 or $PMePh_2$ to a solution of **2a** in CH_2Cl_2 affords the yellow compounds of formula $Os_3(CO)_{10}(CNPr)L$ (**3a**, L = PPh_3; **3b**, L = $PMePh_2$). An X-ray crystal analysis of complex **3a** has been undertaken (Figure 1). The molecule consists of a triangular cluster of osmium atoms with distances Os(1)–Os(2) = 2.9123 (9) Å, Os(1)–Os(3) = 2.8831 (9) Å, and Os(2)–Os(3) = 2.8801 (8) Å. The linear isocyanide ligand occupies an axial coordination site on Os(3) as observed in several other isocyanide metal carbonyl compounds.[7] The PPh_3 ligand is coordinated at the equatorial site of the cluster due to the steric hindrance.[6] These reactions showed that the coordinated acetonitrile ligand in $Os_3(CO)_{10}(CNR)(NCMe)$ (**2**) is labile and easy to be displaced by two-electron donor ligands with the behavior similar to the "lightly stabilized" derivatives $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$.[8-10]

Reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with Propynoic Acid. Treatment of the acetonitrile complexes $Os_3(CO)_{10}(CNR)(NCMe)$ (**2**) with 1.2 equiv or excess (40 equiv) of $HC{\equiv}CCO_2H$ in CH_2Cl_2 at room temperature for 5 h affords the hydrido complexes $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(CNR)$ (**4a**, R = Pr; **4b**, R = Pr^i) in about 60% yield (eq 2). The ^1H NMR spectrum of **4a** shows an acetylenic hydrogen signal at δ 2.38, indicating that the acetylenic group is uncoordinated (C*H* proton for the free ligand appears at δ 3.0).[5] The infrared spectrum shows the $\nu_{C{\equiv}N}$ absorption at 2227 cm^{-1}, which is characteristic of a terminally coordinated isocyanide ligand.[2] The ^1H NMR spectrum of **4a** shows two hydride peaks at δ −15.03 and −15.23 in a 10:3 ratio, which may be attributed to the two isomers with different locations of the isocyanide ligand. The FAB mass spectrum of **4a** shows the molecular ion at *m/z* 992.

In acetonitrile, complex **2** reacts with excess propynoic acid (40 equiv) at room temperature overnight to afford



(2)

not only the hydrido complex **4** but also the bridging aminocarbyne complexes $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHR)$ (**5a**, R = Pr; **5b**, R = Pr^i) along with an unidentified trace product (eq 2). The ^1H NMR spectrum of **5a** does not show any peak of a bridging hydride as observed in **4a**, whereas it shows a bridging aminocarbyne peak (*H*N) at δ 9.07. Also a downfield shift of the acetylenic proton at δ 3.16 was observed. The FAB mass spectrum of **5a** shows a molecular ion at *m/z* 992 indicating that complexes **4a** and **5a** are isomers. Complex **5** exists as two isomers due to the restricted rotation about the C–N bond in the bridging aminocarbyne in solution.[3] However, due to the rapid rotation about the RC(O)–O bond in the carboxylate group, two isomers show the same ^1H and ^{13}C NMR spectra at room temperature. At −60 °C, the ^1H NMR spectrum of the isomers of $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHPr)$ (**5a**) shows two broad peaks at δ 9.23 and 9.20 in CD_2Cl_2 assigned to *H*N of the bridging aminocarbyne of each isomer, respectively. The reaction of **2** with propynoic acid experiences a strong solvent effect. In CH_2Cl_2, the reaction is completed within 5 h to give only the hydrido complex **4**, suggesting that the ionized proton of propynoic acid preferentially attacks the Os atom to give the bridging hydrido osmium derivative. However in acetonitrile, the reaction needs more time to go to completion, and the products consist of the hydrido complex **4** and the bridging aminocarbyne complex **5**. This suggests that, due to the high concentration of the surrounding acetonitrile, the probability of propynoic acid to displace the coordinated acetonitrile is less. Therefore, it creates an opportunity for the isocyanide ligand to react with the proton and transform to the bridging aminocarbyne derivative. The solvent effect on these reactions is closely related to the solvent effect on the rate of isomerization of $H_2Os_3(CO)_{10}(CNR)$ to $HOs(CO)_{10}(\mu\text{-}CNHR)$.[2,11]

An X-ray crystal analysis of complex **5a** (Figure 2) was undertaken in order to obtain unambiguous information on its molecular stereochemistry. The three Os atoms define an isosceles triangle, with Os(1) and Os(3) bridged by both an aminocarbyne group and an unique unidentate carboxylate ligand. Pseudooctahedral geometry is observed around both metals. The doubly bridged Os(1)–Os(3) vector (3.1443 (13) Å) is longer than the nonbridged bonds (Os(1)–Os(2) = 2.8578 (16) Å and Os(2)–Os(3) = 2.8712 (14) Å), indicating that the metal–metal bond has been cleaved with probably only slight interaction. The aminocarbyne ligand is structurally similar to those found in the clusters $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}CNMe_2)$[12] and $(\mu\text{-}H)Os$-

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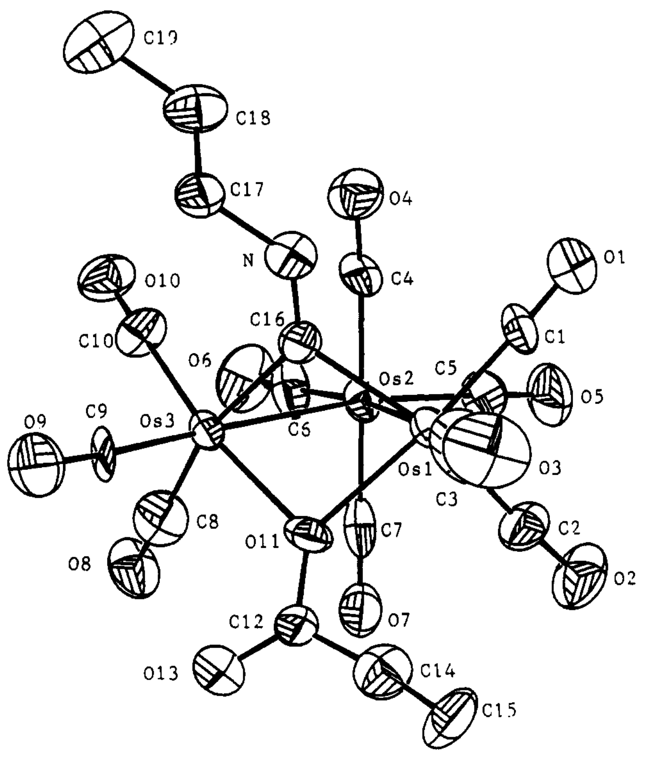

Figure 2. ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHPr)$ (**5a**).

$(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}H_2CNMe_2)(\mu\text{-}SPh)$[13] with C(16)–N = 1.29 (3) Å. The C(14)–C(15) bond with a length of 1.17 (4) Å is in the range of a typical triple bond.

The formation of complexes **5** and **4** shown in eq 2 has three unique features compared to the previous observations by Arce and Deeming in the preparation of the related complex $Os_3H(CO)_{10}(CH{\equiv}CCO_2)$ via $Os_3(CO)_{10}(NCMe)_2$ as starting material.[4,5] First, the coordination mode of carboxylate ion on $Os_3H(CO)_{10}(CH{\equiv}CCO_2)$ is the bidentate-O,O′ coordination, while the bridging aminocarbyne complex **5** bears the bridging unidentate-O coordination mode. Although the carboxylate ion RCO_2^- exhibits a range of different coordination modes ranging from unidentate to quadridentate on transition metal,[14] it is quite rare to have the bridging unidentate-O coordination type on bimetal centers.[15] A bidentate-O,O′ carboxylate group tends to occupy two axial coordination sites and the O–Os–Os angles are near 90° as in $Os_3H(CO)_{10}(CH{\equiv}CCO_2)$,[4,5] but for complex **5** occupied with a bridging aminocarbyne group above the Os_3 plane, the unidentate mode occurs probably because it is difficult for a $\mu\text{-}\eta^2\text{-}O_2CR$ ligand to span coordination sites and still maintain optimum band angles. Second, the structure of complex **4** is suggested to bear the similar bridging unidentate ($\mu_2\text{-}\eta^1$-oxo) carboxylate ligand. The IR spectrum of **4a** shows two absorption peaks in the ν_{CO_2} stretching region at 1614 and 1303 cm^{-1}, while the corresponding peaks for $CH{\equiv}CCO_2Na$ are at 1548 and 1349 cm^{-1}. From the established criterion [$\Delta_{unidentate} > \Delta_{ionic}$; Δ is the separation between $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$] reported by Deacon,[16] complex **4** is therefore likely to have a unidentate carboxylate group similar to that of **5**. The axial-coordinated isocyanide ligand may play an important role in determining the formation of this coordination mode. Third, the formation of complex **5** shows that the coordinated isocyanide accepts a proton from propynoic acid to transform to the bridging aminocarbyne as a three-electron donor. The osmium cluster is doubly bridged, and cleavage of the Os–Os bond takes place instead of CO elimination, while in the case of $Os_3H(CH{\equiv}CCO_2)(CO)_{10}$ the bridging Os–Os bond remains as a normal single bond.[4,5]

Table I. Crystal and Intensity Collection Data for $Os_3(CO)_{10}(CNPr)(PPh_3)$ (3a) and $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}CNHPr)$ (5a)

	3a	**5a**
formula	$C_{32}H_{22}NO_{10}POs_3$	$C_{17}H_9NO_{12}Os_3$
fw	1182.10	989.85
space group	$P\bar{1}$	$P2_12_12_1$
a, Å	11.4611 (4)	9.4241 (23)
b, Å	11.6963 (19)	15.414 (4)
c, Å	14.9661 (22)	15.972 (3)
α, deg	93.635 (12)	
β, deg	73.633 (11)	
γ, deg	117.325 (11)	
V, Å^3	1705.0 (4)	2320.2 (9)
D_{calc}, g cm^{-3}	2.303	2.834
Z	2	4
cryst dimens, mm	0.25 × 0.38 × 0.31	0.31 × 0.31 × 0.19
abs coeff μ(Mo Kα), cm^{-1}	112.6	164.7
temp	room temp	room temp
radiation	Mo Kα	Mo Kα
2θ(max), deg	49.8	44.9
scan type	θ/2θ	θ/2θ
tot. no. of reflcns	6317	3360
no. of obsd reflcns $F_o > 2\sigma(F_o)$	4501	2570
no. of obsd variables	424	298
R	0.042	0.032
R_w	0.051	0.035
Δ(ρ), e Å^{-3}	2.830	1.240
Δ/σ_{max}	0.140	0.724
GOF	2.16	1.54

In conclusion, due to the labile nitrile ligand, the complexes $Os_3(CO)_{10}(CNR)(NCMe)$ (**2**) exhibit high reactivity toward ligand-substitution reactions. The labile complex **2** would therefore be a useful precursor to incorporate interested ligands into the osmium isocyanide cluster and subsequently to provide the opportunity for studying the subtle different reactivities between $Os_3(CO)_{11}(CNR)$ and $Os_3(CO)_{12}$. In the reaction of **2** with propynoic acid, the formation of **5** demonstrates some impressive features including the transformation of the coordinated isocyanide to the bridging aminocarbyne and a unique unidentate carboxylate coordination mode along with the cleavage of the double-bridged Os–Os bond instead of CO elimination.

Experimental Section

General Data. The complexes $Os_3(CO)_{11}(CNPr)$, $Os_3(CO)_{11}(CNPr^i)$, and $Os_3(CO)_{11}(CNPh)$ were prepared previously.[3] Other reagents were purchased from commercial sources and were used as received. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by stirring over Na/benzophenone (tetrahydrofuran, ether) or CaH_2 (hexane, CH_2Cl_2, CH_3CN) and were freshly distilled prior to use. IR spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. NMR spectra were obtained on a Brucker MSL-200, an AC-200, or an AMX-500 FT NMR spectrometer, and mass spectra were recorded on a VG 70-250S mass spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The ^{31}P chemical shifts are referenced with respect to external 85% H_3PO_4.

Synthesis of $Os_3(CO)_{10}(CNR)(NCMe)$ (R = Pr, Pr^i, Ph). All compounds were prepared similarly. A typical preparation is listed here for $Os_3(CO)_{10}(CNPh)(NCMe)$ (**2c**): A solution of

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Table II. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for $Os_3(CO)_{10}(CNPr)(PPh_3)$ (3a)

atom	*x*	*y*	*z*	B_{iso}[a]
Os(1)	0.70114 (6)	0.28217 (5)	0.40928 (4)	3.43 (3)
Os(2)	0.82135 (6)	0.31936 (5)	0.20746 (3)	3.03 (3)
Os(3)	0.57820 (6)	0.34843 (6)	0.29084 (4)	3.64 (3)
P	1.0135 (4)	0.2831 (3)	0.19090 (23)	3.08 (17)
N	0.3847 (14)	0.0534 (13)	0.2697 (10)	5.4 (8)
O(1)	0.5337 (15)	−0.0066 (10)	0.3823 (8)	6.8 (9)
O(2)	0.8989 (17)	0.5673 (13)	0.4286 (10)	9.6 (11)
O(3)	0.4761 (12)	0.2797 (12)	0.5772 (7)	6.0 (7)
O(4)	0.8567 (15)	0.1988 (14)	0.5043 (8)	7.3 (10)
O(5)	1.0041 (13)	0.6091 (10)	0.2194 (9)	7.1 (8)
O(6)	0.6488 (12)	0.0361 (10)	0.1735 (8)	5.8 (7)
O(7)	0.8353 (15)	0.3913 (14)	0.0124 (8)	7.7 (11)
O(8)	0.7504 (16)	0.6344 (12)	0.3154 (11)	9.5 (11)
O(9)	0.3377 (13)	0.3612 (14)	0.4363 (8)	7.3 (9)
O(10)	0.5394 (17)	0.4075 (17)	0.1093 (10)	9.3 (13)
C(1)	0.5967 (19)	0.1008 (16)	0.3872 (10)	5.2 (11)
C(2)	0.8260 (20)	0.4647 (19)	0.4154 (11)	6.1 (11)
C(3)	0.5603 (16)	0.2808 (15)	0.5146 (10)	4.8 (9)
C(4)	0.8027 (17)	0.2320 (17)	0.4647 (10)	5.0 (10)
C(5)	0.9330 (17)	0.5009 (16)	0.2198 (10)	4.7 (9)
C(6)	0.7085 (14)	0.1405 (15)	0.1914 (10)	4.0 (8)
C(7)	0.8359 (18)	0.3655 (17)	0.0845 (12)	5.3 (12)
C(8)	0.6903 (20)	0.5283 (18)	0.3044 (13)	6.3 (11)
C(9)	0.4263 (16)	0.3534 (15)	0.3815 (11)	4.6 (10)
C(10)	0.5583 (19)	0.3875 (19)	0.1779 (14)	6.1 (12)
C(11)	0.4569 (16)	0.1549 (16)	0.2792 (10)	4.4 (9)
C(12)	0.2984 (22)	−0.0807 (18)	0.2607 (16)	8.0 (13)
C(13)	0.288 (5)	−0.106 (3)	0.166 (3)	20.5 (41)
C(14)	0.324 (6)	−0.056 (4)	0.095 (3)	18.7 (50)
C(21)	0.9972 (15)	0.1606 (13)	0.2706 (9)	3.4 (7)
C(22)	1.1004 (15)	0.1754 (15)	0.3076 (11)	4.6 (9)
C(23)	1.0865 (19)	0.0777 (20)	0.3636 (12)	6.2 (13)
C(24)	0.9656 (19)	−0.0415 (16)	0.3832 (11)	5.0 (10)
C(25)	0.8658 (19)	−0.0555 (15)	0.3475 (12)	5.1 (10)
C(26)	0.8805 (15)	0.0436 (14)	0.2931 (10)	4.0 (8)
C(31)	1.1643 (14)	0.4259 (13)	0.2027 (9)	3.4 (7)
C(32)	1.2805 (15)	0.4922 (14)	0.1292 (10)	4.2 (8)
C(33)	1.3913 (18)	0.5993 (16)	0.1429 (12)	5.7 (10)
C(34)	1.3923 (19)	0.6448 (16)	0.2297 (13)	5.9 (11)
C(35)	1.2768 (19)	0.5825 (16)	0.3037 (11)	5.6 (11)
C(36)	1.1644 (16)	0.4752 (16)	0.2913 (10)	4.9 (9)
C(41)	1.0785 (14)	0.2303 (12)	0.0766 (9)	3.4 (7)
C(42)	1.0459 (21)	0.2454 (22)	−0.0021 (11)	7.3 (16)
C(43)	1.1042 (25)	0.216 (3)	−0.0860 (11)	9.5 (22)
C(44)	1.1928 (20)	0.1654 (18)	−0.0964 (11)	6.1 (11)
C(45)	1.230 (3)	0.1523 (20)	−0.0195 (13)	8.4 (17)
C(46)	1.1692 (22)	0.1851 (20)	0.0649 (11)	6.9 (14)

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

Table III. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHPr)$ (5a)

atom	*x*	*y*	*z*	B_{iso}[a]
Os(1)	0.63783 (12)	0.67454 (6)	0.33396 (5)	2.72 (4)
Os(2)	0.91906 (11)	0.61425 (7)	0.30087 (6)	2.82 (4)
Os(3)	0.71264 (11)	0.55127 (6)	0.18345 (5)	2.27 (4)
N	0.6244 (20)	0.7444 (12)	0.1540 (10)	2.9 (9)
O(1)	0.7478 (24)	0.8512 (11)	0.3676 (10)	5.7 (10)
O(2)	0.6760 (22)	0.6235 (13)	0.5212 (9)	5.9 (11)
O(3)	0.3375 (20)	0.7349 (14)	0.3460 (12)	7.1 (12)
O(4)	0.9496 (18)	0.7769 (12)	0.1936 (9)	4.7 (9)
O(5)	1.0454 (23)	0.6959 (13)	0.4573 (10)	6.3 (11)
O(6)	1.1804 (20)	0.5251 (14)	0.2198 (11)	6.8 (12)
O(7)	0.8309 (20)	0.4533 (11)	0.3996 (9)	4.5 (9)
O(8)	0.8460 (22)	0.3689 (11)	0.2062 (10)	5.5 (10)
O(9)	0.4795 (20)	0.4936 (13)	0.0651 (9)	5.2 (9)
O(10)	0.9109 (20)	0.5897 (12)	0.0449 (9)	4.8 (9)
O(11)	0.5823 (17)	0.5445 (9)	0.2941 (8)	3.0 (7)
O(13)	0.4893 (20)	0.4138 (11)	0.2869 (9)	4.4 (9)
C(1)	0.7024 (27)	0.7833 (15)	0.3563 (13)	3.1 (11)
C(2)	0.6580 (33)	0.6395 (16)	0.4526 (14)	4.3 (13)
C(3)	0.4445 (26)	0.7102 (19)	0.3455 (18)	5.6 (16)
C(4)	0.9374 (25)	0.7161 (14)	0.2363 (13)	2.9 (11)
C(5)	0.9984 (29)	0.6686 (19)	0.4002 (14)	4.3 (13)
C(6)	1.0838 (29)	0.5586 (18)	0.2539 (14)	4.7 (13)
C(7)	0.8694 (26)	0.5165 (16)	0.3602 (12)	3.3 (11)
C(8)	0.7913 (25)	0.4389 (15)	0.1979 (14)	3.6 (11)
C(9)	0.5610 (27)	0.5147 (17)	0.1109 (12)	3.7 (12)
C(10)	0.8312 (24)	0.5758 (18)	0.0944 (13)	3.5 (13)
C(12)	0.4973 (28)	0.4846 (16)	0.3199 (13)	3.8 (12)
C(14)	0.4109 (29)	0.5090 (18)	0.3906 (14)	4.2 (13)
C(16)	0.6437 (25)	0.6787 (15)	0.2023 (12)	2.8 (11)
C(17)	0.6270 (29)	0.7477 (16)	0.0643 (13)	3.5 (12)
C(18)	0.7581 (28)	0.7909 (17)	0.0275 (15)	4.3 (13)
C(19)	0.7564 (33)	0.7957 (21)	−0.0705 (15)	6.0 (17)
C(15)	0.3321 (33)	0.5227 (19)	0.4458 (13)	5.4 (16)

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

$Os_3(CO)_{11}(CNPh)$ (84 mg, 0.09 mmol) in CH_2Cl_2 (80 mL) and acetonitrile (1 mL) was treated with a solution of Me_3NO (8 mg, 0.11 mol) in 20:100 CH_3CN/CH_2Cl_2. 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 recrystallized from hexane/CH_2Cl_2/CH_3CN to give **2c** (69 mg, 0.07 mmol, 81%). Anal. Calcd for $C_{19}H_8N_2O_{10}Os_3$: C, 22.93; H, 0.81. Found: C, 23.69; H, 0.74. IR (CH_2Cl_2): ν_{CN} = 2160 (w), ν_{CO} = 2073 (w), 2024 (vs), 1986 (s), 1963 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.39–7.27 (m, Ph), 2.66 (s, CH_3). MS (FAB): *m/z* 997 (M^+), 956 (M^+ − NCMe), 928 (M^+ − NCMe − CO), 900 (M^+ − NCMe − 2CO), 872 (M^+ − NCMe − 3CO), 844 (M^+ − NCMe − 4CO), 816 (M^+ − NCMe − 5CO), 788 (M^+ − NCMe − 6CO).

$Os_3(CO)_{10}(CNPr)(NCMe)$ (**2a**): yield 78%. Anal. Calcd for $C_{16}H_{10}N_2O_{10}Os$: C, 20.00; H, 1.05. Found: C, 20.11; H, 1.08. IR (CH_2Cl_2): ν_{CN} = 2198 (w) cm^{-1}, ν_{CO} = 2076 (vw), 2023 (vs), 1986 (s), 1963 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.89 (t, 2 H, $CNCH_2$), 2.64 (s, 3 H, $NCCH_3$), 1.71 (m, 2 H, CH_2CH_3), 1.01 (t, 3 H, CH_3). MS (FAB): *m/z* 963 (M^+), 922 (M^+ − NCMe), 894 (M^+ − NCMe − CO), 866 (M^+ − NCMe − 2CO), 838 (M^+ − NCMe − 3CO), 810 (M^+ − NCMe − 4CO).

$Os_3(CO)_{10}(CNPr^i)(NCMe)$ (**2b**): yield 76%. IR (CH_2Cl_2): ν_{CN} = 2187 (w), ν_{CO} = 2076 (vw), 2022 (vs), 1987 (s), 1963 (m), cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.32 (m, 1 H, *CH*), 2.64 (s, 3 H, $NCCH_3$), 1.35 (d, 6 H, CH_3).

Carbonylation of 2. Carbon monoxide was bubbled through the solution of **2** in CH_2Cl_2 at room temperature. After 1 h, the IR data indicated that the conversion of **2** to **1** had taken place in almost quantitative yield.

Reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with Phosphine. A solution of $Os_3(CO)_{11}(CNPr)$ (84 mg, 0.09 mmol) in CH_2Cl_2 (80 mL) and acetonitrile (1 mL) was treated with a solution of Me_3NO (8 mg, 0.11 mmol) in 20:100 CH_3CN/CH_2Cl_2 (3 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 dissolved in 80 mL of CH_2Cl_2. The resulting solution of $Os_3(CO)_{10}(CNPr)(NCMe)$ was treated with PPh_3 (28 mg, 0.11 mmol) and stirred for 5 h. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with hexane as eluent to give $Os_3(CO)_{10}(CNPr)(PPh_3)$ (**3a**) (78 mg, 0.07 mmol, 75%). Anal. Calcd for $C_{32}H_{22}NO_{10}POs_3$: C, 32.49; H, 1.86. Found: C, 32.47; H, 1.84. IR (CH_2Cl_2): ν_{CN} = 2198 (w), ν_{CO} = 2079 (m), 2032 (vs), 2020 (m), 1998 (s), 1972 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.47–7.37 (m, 15 H, Ph), 3.91 (t, 2 H, NCH_2), 1.71 (m, 2 H, CH_2CH_3), 0.99 (t, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 185.1 (br, CO), 175.4 (br, CO), 136.6, 135.6, 133.2, 133.0, 130.2, 128.3, 128.1 (Ph and CN), 46.8 ($CNCH_2$), 22.6 (CH_2CH_3), 11.0 (CH_3). ^{31}P NMR ($CDCl_3$): δ −0.33 (PPh_3).

Complex $Os_3(CO)_{10}(CNPr)(PMePh_2)$ (**3b**) was obtained under reaction conditions similar to those of **3a**. **3b**: yield 60%. IR (*n*-hexane): ν_{CN} = 2197 (w), ν_{CO} = 2079 (m), 2030 (vs), 2017 (m), 1999 (s), 1969 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.54–7.39 (m, 10 H, Ph), 3.88 (t, 2 H, NCH_2), 2.40 (d, 3 H, PCH_3), 1.70 (m, 2 H, CH_2CH_3), 0.99 (t, 3 H, CH_3). ^{31}P NMR ($CDCl_3$): δ −20.2. MS (FAB): *m/z* 1122 (M^+), 1094 (M^+ − CO), 1066 (M^+ − 2CO), 1038 (M^+ − 3CO), 1010 (M^+ − 4CO), 982 (M^+ − 5CO), 954 (M^+ − 6CO).

Reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with Propynoic Acid in CH_2Cl_2. A solution of $Os_3(CO)_{11}(CNPr)$ (71 mg, 0.08 mmol) in CH_2Cl_2 (70 mL) and acetonitrile (1 mL) was treated with a solution of Me_3NO (9 mg, 0.09 mmol) in 20:100 CH_3CN/CH_2Cl_2 (3 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 resolved in 70 mL of CH_2Cl_2. The resulting solution of $Os_3(CO)_{10}(CNPr)(NCMe)$ was treated with $CH{\equiv}CCO_2H$ (5 μL, 0.08 mmol) and stirred for

Table IV. Selected Bond Distances and Angles for $Os_3(CO)_{10}(CNPr)(PPh_3)$ (3a)

(a) Bond Distances (Å)

Os(1)–Os(2)	2.9123 (9)	Os(1)–Os(3)	2.8831 (9)
Os(1)–C(1)	1.961 (17)	Os(1)–C(2)	1.965 (19)
Os(1)–C(3)	1.906 (14)	Os(1)–C(4)	1.903 (18)
Os(2)–Os(3)	2.8801 (8)	Os(2)–P	2.373 (4)
Os(2)–C(5)	1.941 (16)	Os(2)–C(6)	1.932 (15)
Os(2)–C(7)	1.891 (17)	Os(3)–C(8)	1.931 (19)
Os(3)–C(9)	1.904 (15)	Os(3)–C(10)	1.879 (21)
Os(3)–C(11)	2.070 (17)	N–C(11)	1.122 (22)
N–C(12)	1.442 (23)	O(1)–C(1)	1.136 (20)
O(2)–C(2)	1.148 (23)	O(3)–C(3)	1.136 (17)
O(4)–C(4)	1.158 (22)	O(5)–C(5)	1.148 (20)
O(6)–C(6)	1.152 (18)	O(7)–C(7)	1.141 (21)
O(8)–C(8)	1.138 (23)	O(9)–C(9)	1.148 (18)
O(10)–C(10)	1.17 (3)		

(b) Bond Angles (deg)

Os(2)–Os(1)–Os(3)	59.596 (21)	Os(2)–Os(1)–C(1)	85.0 (4)
C(12)–C(13)–C(14)	141 (3)	Os(2)–Os(1)–C(2)	87.9 (4)
Os(2)–Os(1)–C(3)	148.2 (5)	Os(2)–Os(1)–C(4)	109.2 (4)
Os(3)–Os(1)–C(1)	88.1 (5)	Os(3)–Os(1)–C(2)	91.7 (6)
Os(3)–Os(1)–C(3)	88.6 (5)	Os(3)–Os(1)–C(4)	168.6 (4)
C(1)–Os(1)–C(2)	171.9 (6)	C(1)–Os(1)–C(3)	94.7 (7)
C(1)–Os(1)–C(4)	88.5 (7)	C(2)–Os(1)–C(3)	93.5 (6)
C(2)–Os(1)–C(4)	90.1 (8)	P–C(21)–C(22)	123.4 (11)
C(3)–Os(1)–C(4)	102.6 (7)	P–C(21)–C(26)	120.5 (11)
Os(1)–Os(2)–Os(3)	59.697 (22)	Os(1)–Os(2)–P	101.53 (8)
Os(1)–Os(2)–C(5)	89.1 (4)	Os(1)–Os(2)–C(6)	92.3 (4)
Os(1)–Os(2)–C(7)	153.9 (5)	Os(3)–Os(2)–P	161.22 (8)
Os(3)–Os(2)–C(5)	89.6 (4)	Os(3)–Os(2)–C(6)	89.8 (4)
Os(3)–Os(2)–C(7)	94.3 (5)	P–Os(2)–C(5)	89.5 (5)
P–Os(2)–C(6)	91.7 (4)	P–Os(2)–C(7)	104.4 (5)
C(5)–Os(2)–C(6)	177.9 (7)	C(5)–Os(2)–C(7)	88.0 (7)
C(6)–Os(2)–C(7)	90.0 (7)	Os(1)–Os(3)–Os(2)	60.707 (21)
Os(1)–Os(3)–C(8)	88.7 (6)	P–C(31)–C(32)	124.0 (10)
Os(1)–Os(3)–C(9)	100.7 (5)	P–C(31)–C(36)	118.9 (10)
Os(1)–Os(3)–C(10)	156.5 (5)	Os(1)–Os(3)–C(11)	90.6 (4)
Os(2)–Os(3)–C(8)	90.0 (5)	Os(2)–Os(3)–C(9)	161.4 (5)
Os(2)–Os(3)–C(10)	95.8 (5)	Os(2)–Os(3)–C(11)	90.4 (4)
C(8)–Os(3)–C(9)	89.7 (7)	C(8)–Os(3)–C(10)	92.0 (9)
C(8)–Os(3)–C(11)	178.8 (7)	C(9)–Os(3)–C(10)	102.7 (7)
C(9)–Os(3)–C(11)	89.6 (6)	C(10)–Os(3)–C(11)	89.0 (8)
Os(2)–P–C(21)	118.5 (4)	Os(2)–P–C(31)	113.6 (4)
Os(2)–P–C(41)	116.0 (5)	C(21)–P–C(31)	103.3 (7)
C(21)–P–C(41)	100.6 (6)	P–C(41)–C(42)	122.4 (11)
C(31)–P–C(41)	102.6 (6)	P–C(41)–C(46)	121.0 (12)
C(11)–N–C(12)	175.2 (19)	Os(3)–C(11)–N	173.9 (15)
N–C(12)–C(13)	112.7 (20)		

Table V. Selected Bond Distances and Angles for $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHPr)$ (5a)

(a) Bond Distances (Å)

Os(1)–Os(2)	2.8578 (16)	O(3)–C(3)	1.08 (3)
Os(1)–Os(3)	3.1443 (13)	O(4)–C(4)	1.17 (3)
Os(1)–O(11)	2.167 (14)	O(5)–C(5)	1.10 (3)
Os(1)–C(1)	1.819 (23)	O(6)–C(6)	1.18 (3)
Os(1)–C(2)	1.979 (22)	O(7)–C(7)	1.21 (3)
Os(1)–C(3)	1.912 (24)	O(8)–C(8)	1.20 (3)
Os(1)–C(16)	2.105 (20)	O(9)–C(9)	1.11 (3)
Os(2)–Os(3)	2.8712 (14)	O(10)–C(10)	1.11 (3)
Os(2)–C(4)	1.885 (22)	O(11)–C(12)	1.29 (3)
Os(2)–C(5)	1.943 (23)	O(13)–C(12)	1.21 (3)
Os(2)–C(6)	1.93 (3)	C(12)–C(14)	1.44 (3)
Os(2)–C(7)	1.84 (3)	C(14)–C(15)	1.17 (4)
Os(3)–O(11)	2.155 (14)	C(17)–C(18)	1.52 (4)
Os(3)–C(8)	1.899 (23)	Os(3)–C(9)	1.924 (22)
Os(3)–C(10)	1.848 (21)	Os(3)–C(16)	2.090 (23)
O(1)–C(1)	1.15 (3)	N–C(17)	1.43 (3)
O(2)–C(2)	1.14 (3)	N–C(16)	1.29 (3)

(b) Bond Angles (deg)

Os(2)–Os(1)–Os(3)	56.92 (3)	O(11)–Os(3)–C(10)	170.4 (9)
Os(2)–Os(1)–O(11)	82.5 (4)	O(11)–Os(3)–C(16)	75.5 (7)
Os(2)–Os(1)–C(1)	91.5 (8)	C(8)–Os(3)–C(9)	95.5 (10)
Os(2)–Os(1)–C(2)	90.0 (8)	C(8)–Os(3)–C(10)	92.5 (11)
Os(2)–Os(1)–C(3)	174.3 (9)	C(8)–Os(3)–C(16)	164.0 (8)
Os(2)–Os(1)–C(16)	78.5 (6)	C(9)–Os(3)–C(10)	92.6 (10)
Os(3)–Os(1)–O(11)	43.2 (4)	C(9)–Os(3)–C(16)	97.5 (10)
Os(3)–Os(1)–C(1)	129.2 (7)	C(10)–Os(3)–C(16)	96.1 (10)
Os(3)–Os(1)–C(2)	123.1 (7)	C(16)–N–C(17)	128.6 (19)
Os(3)–Os(1)–C(3)	117.5 (9)	Os(3)–Os(1)–C(16)	41.3 (6)
O(11)–Os(1)–C(1)	172.3 (9)	Os(1)–O(11)–Os(3)	93.4 (5)
O(11)–Os(1)–C(2)	93.0 (8)	Os(1)–O(11)–C(12)	135.9 (14)
O(11)–Os(1)–C(3)	93.7 (10)	Os(3)–O(11)–C(12)	130.5 (14)
O(11)–Os(1)–C(16)	75.0 (7)	C(1)–Os(1)–C(2)	91.8 (10)
C(1)–Os(1)–C(3)	92.0 (12)	C(1)–Os(1)–C(16)	99.2 (9)
C(2)–Os(1)–C(3)	94.5 (12)	C(2)–Os(1)–C(16)	164.2 (10)
C(3)–Os(1)–C(16)	96.5 (11)	Os(1)–Os(2)–Os(3)	66.57 (4)
Os(1)–Os(2)–C(4)	85.2 (7)	Os(1)–Os(2)–C(5)	93.8 (8)
Os(1)–Os(2)–C(6)	164.7 (7)	O(11)–C(12)–O(13)	123.0 (21)
Os(1)–Os(2)–C(7)	86.3 (7)	O(11)–C(12)–C(14)	114.4 (21)
Os(3)–Os(2)–C(4)	89.2 (7)	O(13)–C(12)–C(14)	122.6 (23)
Os(3)–Os(2)–C(5)	160.0 (8)	C(12)–C(14)–C(15)	173 (3)
Os(3)–Os(2)–C(6)	98.1 (7)	Os(1)–C(16)–Os(3)	97.1 (9)
Os(3)–Os(2)–C(7)	83.5 (7)	Os(1)–C(16)–N	128.2 (16)
C(4)–Os(2)–C(5)	93.0 (11)	Os(3)–C(16)–N	134.3 (15)
C(4)–Os(2)–C(6)	94.8 (11)	N–C(17)–C(18)	114.6 (20)
C(5)–Os(2)–C(6)	101.5 (11)	C(5)–Os(2)–C(7)	91.8 (10)
C(6)–Os(2)–C(7)	92.4 (11)	Os(1)–Os(3)–Os(2)	56.51 (3)
Os(1)–Os(3)–O(11)	43.5 (4)	Os(1)–Os(3)–C(8)	123.1 (6)
Os(1)–Os(3)–C(9)	118.1 (8)	Os(1)–Os(3)–C(10)	126.9 (8)
Os(1)–Os(3)–C(16)	41.6 (5)	Os(2)–Os(3)–O(11)	82.3 (4)
Os(2)–Os(3)–C(8)	88.0 (6)	Os(2)–Os(3)–C(9)	174.6 (7)
Os(2)–Os(3)–C(10)	91.4 (7)	Os(2)–Os(3)–C(16)	78.4 (6)
O(11)–Os(3)–C(8)	94.5 (9)	O(11)–Os(3)–C(9)	93.2 (8)

5 h. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with 50:50 CH_2Cl_2/hexane as eluent to give $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(CNPr)$ (**4a**) (47 mg, 0.05 mmol, 64%). If this reaction was carried out with excess propynoic acid (40 equiv), a similar result (61%) was obtained. Anal. Calcd for $C_{17}H_9NO_{12}Os_3$: C, 20.63; H, 0.92. Found: C, 20.75; H, 0.78. IR (CH_2Cl_2): $\nu_{CN} = 2227$ (w), $\nu_{CO} = 2111$ (w), 2082 (vs), 2067 (s), 2040 (m), 2020 (s), 1980 (br) cm^{-1} [$\nu_{CO_2} = 1614$, 1303 cm^{-1} in KBr, while ν_{CO_2} for $CH{\equiv}CCO_2Na$ = 1548, 1349 cm^{-1} in KBr]. ^1H NMR ($CDCl_3$): δ 3.97, 3.85 (t, 2 H, CH_2, $J_{HH} = 6.9$ Hz, two isomers in a 3:10 ratio), 2.43 (s, 1 H, $HC{\equiv}C$), 1.75 (m, 2 H, CH_2), 1.00 (t, 3 H, CH_3, $J_{HH} = 7.3$ Hz), −15.03, −15.23 (s, 1 H, Os–H–Os, two isomers in a 10:3 ratio). ^{13}C NMR ($CDCl_3$): δ 184.44, 182.35, 181.13, 179.44, 176.29, 175.25, 174.38, 174.01, 173.33, 173.25, 173.09, 172.93, 171.23, 171.16, 171.07, 170.99, 167.90, 167.83, 167.70, 167.25 (CO, two isomers), 158.17, 157.96 (μ_2-O–CO, two isomers), 114.24, 112.80 ($\mathit{C}{\equiv}N$, two isomers), 75.83 (CH), 69.16, 68.84 ($\mathit{C}{\equiv}CH$, two isomers), 47.30, 47.20 ($CNCH_2$, two isomers), 22.15, 22.06 ($\mathit{C}H_2CH_3$, two isomers), 10.91 ($CH_2\mathit{C}H_3$). MS (FAB): m/z 992 (M^+), 964 ($M^+ - CO$), 936 ($M^+ - 2CO$), 923 ($M^+ - CNPr$), 908 ($M^+ - 3CO$), 895 ($M^+ - CO - CNPr$), 867 ($M^+ - 2CO - CNPr$), 839 ($M^+ - 3CO - CNPr$), 811 ($M^+ - 4CO - CNPr$).

Complex **4b** was obtained under reaction conditions similar to those of **4a** in 62% using $Os_3(CO)_{11}(CNPr^i)$ as a starting material.

$(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(CNPr^i)$ (**4b**): Anal. Calcd for $C_{17}H_9NO_{12}Os$: C, 20.63; H, 0.92. Found: C, 20.70; H, 0.87. IR (CH_2Cl_2): $\nu_{CN} = 2215$ (w), $\nu_{CO} = 2110$ (w), 2081 (vs), 2067 (s), 2040 (m), 2018 (s), 1977 (br) cm^{-1} [$\nu_{CO_2} = 1620$, 1301 cm^{-1} in KBr]. ^1H NMR ($CDCl_3$): δ 4.50, 4.30 (m, 1 H, $C\mathit{H}Me_2$, two isomers in a 2:10 ratio), 2.43, 2.42 (s, 1 H, $HC{\equiv}C$, two isomers in a 10:2 ratio), 1.41 (d, 6 H, CH_3, $J_{HH} = 6.3$ Hz), −15.05, −15.22 (s, 1 H, Os–H–Os, two isomers in a 10:2 ratio). MS (EI): m/z 992 (M^+), 964 ($M^+ - CO$), 949 ($M^+ - CHMe_2$).

Reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with Propynoic Acid in Acetonitrile. A solution of $Os_3(CO)_{11}(CNPr)$ (72 mg, 0.08 mmol) in acetonitrile (70 mL) was treated with a solution of Me_3NO (7 mg, 0.09 mmol) in 20:100 CH_3CN/CH_2Cl_2 (3 mL). The mixture was stirred for 30 min at room temperature and filtered through a small silica column. The resulting solution of $Os_3(CO)_{10}(CNPr)(NCMe)$ was treated with $CH{\equiv}CCO_2H$ (0.20 mL, 3.26 mmol) and stirred for overnight. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with 50:50 CH_2Cl_2/hexane as eluent to give $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHPr)$ (**5a**) (10 mg, 0.01 mmol, 14%), **4a** (9 mg, 0.009 mmol, 12%), and an unidentified complex (4 mg). Data for **5a** are as follows. Anal. Calcd for $C_{17}H_9NO_{12}Os$: C, 20.61; H, 0.91. Found: C, 20.71; H, 0.91. IR (CH_2Cl_2): $\nu_{CO} = 2101$ (w), 2068 (vs), 2051 (s), 2016 (vs), 1991 (s), 1970 (m) cm^{-1} [$\nu_{CO_2} = 1653$, 1259 cm^{-1} in KBr]. ^1H NMR ($CDCl_3$): δ 9.07 (br, 1 H, NH [δ 9.23, 9.20 at −60 °C in CD_2Cl_2]), 3.73, 3.55 (m, CH_aH_b,

$J_{H_aH_b}$ = 12.8 Hz, $J_{H_aH_N}$ = 3.4 Hz, $J_{H_bH_N}$ = 6.7 Hz), 3.16 (s, 1 H, HC≡C), 1.91 (m, 2 H, CH_2), 1.11 (t, 3 H, CH_3, J_{HH} = 7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 269.2 (μ_2-C═NH), 187.9, 187.8, 180.6, 178.2, 177.5, 177.3, 175.9, 175.8, 169.6, 169.2 (CO), 156.3 (μ_2-O–CO), 79.9 (CH), 69.8 (*C*≡CH), 62.5 ($NHCH_2$), 22.1 (CH_2CH_3), 11.4 (CH_2-CH_3). MS (FAB): *m/z* 992 (M^+), 964 ($M^+ - CO$), 936 ($M^+ - 2CO$), 922 ($M^+ - CNHPr$), 908 ($M^+ - 3CO$).

Complex **5b** was obtained under reaction conditions similar to those of **5a** in 12% using $Os_3(CO)_{11}(CNPr^i)$ as starting material. Data for $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHPr^i)$ (**5b**) are as follows. IR (CH_2Cl_2): ν_{CO} = 2100 (w), 2067 (s), 2051 (m), 2014 (s), 1989 (m), 1972 (sh) cm^{-1} [ν_{CO_2} = 1648, 1240 cm^{-1} in KBr]. ^1H NMR ($CDCl_3$): δ 9.08 (d, br 1 H, μ_2-C═NH, J_{HH} = 7.7 Hz), 3.85 (m, 1 H, $CHMe_2$), 3.16 (s, 1 H, HC≡C), 1.49 (d, 3 H, CH_3, J_{HH} = 6.3 Hz), 1.45 (d, 3 H, CH_3, $J_{HH'}$ = 6.7 Hz).

Crystallographic Structure Determination. Crystals of both $Os_3(CO)_{10}(CNPr)(PPh_3)$ (**3a**) and $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHPr)$ (**5a**) were grown from CH_2Cl_2/hexane solutions at −5 °C. Specimens of suitable quality were mounted in a glass capillary and used for measurement of precise cell constants and intensity data collection. All diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.709 30 Å) with θ–2θ 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. Space groups were determined from the systematic absences observed during data collection. The centrosymmetric space group was initially assumed and later confirmed by the results of refinement for **3a**. The systematic absences in the diffraction data of **5a** unambiguously established the space group as $P2_12_12_1$. An empirical absorption correction was applied to each of the data sets. The structures were solved by the heavy-atom method. All remaining non-hydrogen atoms ware 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 using the NRCC SDP program. Crystallographic data for **3a** and **5a** are shown in Table I. Final atomic coordinates, isotropic thermal parameters, and selected bond distances and bond angles for the two complexes are listed in Tables II–V.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

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A Deceptively Simple Case of Selective Hydrogenation of Phenylacetylene to Styrene Catalyzed by a *cis*-Hydrido(η^2-dihydrogen)ruthenium(II) Complex

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Depending on the substrate to metal complex ratio (2, 3, 4), the reaction of the *cis*-hydrido(η^2-dihydrogen)ruthenium(II) complex $[(PP_3)Ru(H)(H_2)]BPh_4$ (**2**) with HC≡CPh in tetrahydrofuran gives the σ-alkenyl $[(PP_3)Ru\{C(H){=}C(H)Ph\}]^+$ (detected spectroscopically), the σ-alkynyl $[(PP_3)Ru(C{\equiv}CPh)]BPh_4{\cdot}THF$ (**6**), or the η^3-butenynyl *E*-$[(PP_3)Ru(\eta^3\text{-}PhC_3CHPh)]BPh_4$ (**3a,b**) [$PP_3 = P(CH_2CH_2PPh_2)_3$]. The latter product is isolated as a 3:1 mixture of geometric isomers displaying a different anchoring mode of the butenynyl ligand to the metal center. The *cis*-hydride(η^2-dihydrogen)ruthenium(II) complex **2** is an active catalyst precursor for the selective hydrogenation of phenylacetylene to styrene. A kinetic study carried out in 1,2-dichloroethane solution shows that the rate of the catalytic hydrogenation reaction is proportional to the initial concentration of the catalyst precursor, second order with respect to dihydrogen pressure, and independent of substrate concentration. At very low concentrations of HC≡CPh (<0.12 M), the order of the catalytic rate with respect to substrate concentration tends to 1. In light of the kinetic study and of the reactivity of **2** toward HC≡CPh, a reaction mechanism is proposed which essentially involves the usual cycle adopted by mono(hydrido)metal catalysts. In fact, unlike the related iron derivative $[(PP_3)Fe(H)(H_2)]BPh_4$ previously investigated, dihydrogen in **2** behaves as a weakly bound ligand which is readily displaced by phenylacetylene. Other ruthenium species, namely the butenynyl complexes **3a,b** and the alkynyl **6**, play a significant role in the catalysis cycle as side intermediates.

Introduction

We have previously reported the synthesis, the characterization, and some chemistry of the *cis*-hydrido(η^2-dihydrogen)ruthenium(II) complexes $[(PP_3)M(H)(H_2)]BPh_4$ [M = Fe (**1**), Ru (**2**); $PP_3 = P(CH_2CH_2PPh_2)_3$].[1-4] The reactivity studies have clearly shown that the solution chemistry of compounds **1** and **2** is dominated by the different metal–dihydrogen bond strengths, which increase

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