Synthesis and Reactivity of Isocyanatogoldtriosmium Clusters †

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Syntheses of $[Os_3(CO)_{11}\{Au(PR_3)\}(NCO)]$ and $[Os_3(CO)_{10}\{Au(PR_3)\}(NCO)]$ (R = Et or Ph) by treating $[Os_3(CO)_{12}]$ with azide anions in the presence of $[Au(PR_3)Cl]$ have been developed. Control experiments indicate that no reaction occurs without $[Au(PR_3)Cl]$, and that $[Au(PR_3)(N_3)]$ is not an intermediate. A similar reaction using nitrite in place of azide gave $[Os_3(CO)_{10}\{Au(PEt_3)\}(NO)]$. $[Os_3(CO)_{10}\{Au(PEt_3)\}(NCO)]$ reacts with nucleophilic reagents (HY) to give $[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCOY)]$ [Y = OH, OMe, $PhCH_2NH$, or $PhCH_2CH(CO_2Me)NH$]; with phosphines to give $[Os_3(CO)_9(PPh_3)\{Au(PR_3)\}(NCO)]$ (R = Et or Ph) and $[Os_3(CO)_9(PEt_3)_3]$; and with BH_3·thf (thf = tetrahydrofuran) to give $[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCHO)]$. Reaction of $[Os_3(CO)_{10}\{Au(PEt_3)\}(NCO)]$ with $PhNPPh_3$ produces $[Os_3(CO)_{10}\{Au(PEt_3)\}(NCNPh)]$, which in turn can react with $PhCH_2NH_2$ to form the compound $[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCNPhNHCH_2Ph)]$ and is reduced to $[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCHNPh)]$ by BH_3·thf.

There are many connections in organometallic chemistry between azides and isocyanates. For instance, co-ordinated azides have been converted into isocyanate ligands by reaction with carbon monoxide under mild conditions.[1] Nucleophilic attack of azide anions on neutral [2] and cationic [3] monomeric metal carbonyls has been shown to produce isocyanate complexes, and it has been suggested that this type of reaction is mechanistically similar to the Curtius rearrangement of organic acyl azides into isocyanates.[4] Furthermore, some low-valent transition metal carbonyls have been treated with organic azides bearing electron-withdrawing substituents to give complexes containing urea or amide ligands, and metal isocyanates have consistently been proposed as intermediates.[5–7] The research reported here is an extension of previous work on the reactions of triosmium clusters with organic azides [8–11] and the syntheses of goldtriosmium clusters.[12,13] While this project was in progress the synthesis and reactivity of $[Os_3(CO)_{10}(\mu\text{-}H)(NCO)]$ was reported in preliminary form; [14] further study of this cluster might provide an interesting comparison.

Results and Discussion

Scheme 1 shows the results of an investigation of the reactions of $[Os_3(CO)_{12}]$ with azide anions in the presence of a phase-transfer catalyst, 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane). Reaction (A) demonstrates that there is no interaction similar to that of azide anions with $[W(CO)_6]$ (see below).[15,‡]

$$[W(CO)_6] + N_3^- \longrightarrow [W(CO)_5(NCO)]^-$$

A reaction does occur, however, when chloro(triethylphosphine)gold(I) $[Au(PEt_3)Cl]$ is added [reaction (C)], and apparently not *via* an azido(phosphine)gold intermediate [reaction (B)]. At elevated temperatures only the decacarbonyl isocyanate (2) is isolated [reaction (D)], presumably because under these conditions the undecacarbonyl isocyanate (1) is decarbonylated to give (2) in high yield [reaction (E)]. The precise mechanism of reactions (C) and (D) cannot be established by these results, but it seems probable that nucleophilic attack on a carbonyl ligand (the accepted mechanism [3] for this type of isocyanate formation) only occurs in the presence of a gold electrophile, or that the attack occurs reversibly and the subsequent irreversible rearrangement and loss of dinitrogen only occur when the electrophile is present.

$$[Os_3(CO)_{12}] + NaN_3 \xrightarrow{i} \text{No reaction} \quad (A)$$

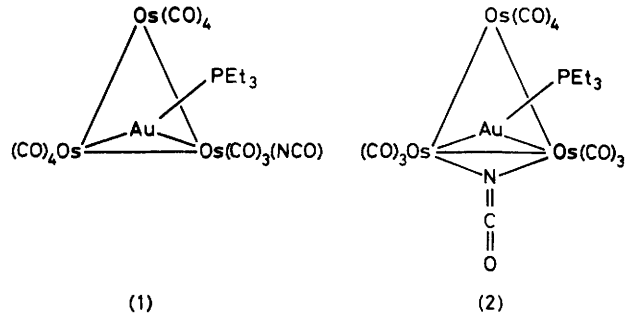
$$[Os_3(CO)_{12}] + [Au(PEt_3)(N_3)] \xrightarrow{ii} \text{No reaction} \quad (B)$$

$$[Os_3(CO)_{12}] + NaN_3 + [Au(PEt_3)Cl] \xrightarrow{iii} [Os_3(CO)_{11}\{Au(PEt_3)\}(NCO)] + [Os_3(CO)_{10}\{Au(PEt_3)\}(NCO)] \quad (C)$$
(1) 20%, (2) 62%

$$[Os_3(CO)_{12}] + NaN_3 + [Au(PEt_3)Cl] \xrightarrow{i} [Os_3(CO)_{10}\{Au(PEt_3)\}(NCO)] \quad (D)$$
(2) 60%

$$[Os_3(CO)_{11}\{Au(PEt_3)\}(NCO)] \xrightarrow{iv} [Os_3(CO)_{10}\{Au(PEt_3)\}(NCO)] \quad (E)$$
(2) 80%

Scheme 1. Reactions of azide anions with $[Os_3(CO)_{12}]$. Reagents and conditions: i, 18-crown-6, thf, 65 °C, 4 h; ii, thf, 20 °C, 15 h; iii, 18-crown-6, thf, 20 °C, 15 h; iv, thf, 65 °C, 1 h



(1) (2)

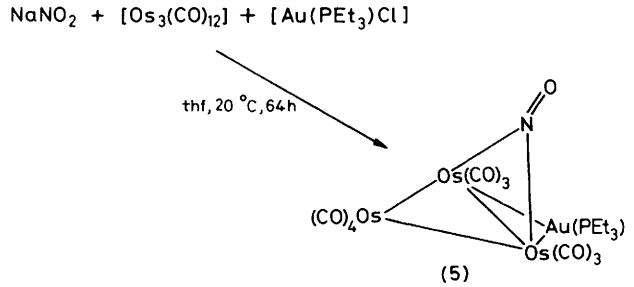
Figure. Possible structures of $[Os_3(CO)_{11}\{Au(PEt_3)\}(NCO)]$ (1) and $[Os_3(CO)_{10}\{Au(PEt_3)\}(NCO)]$ (2)

The assignment of eleven and ten carbonyl groups to (1) and (2), respectively, was not possible from the mass spectra of these products (both spectra indicate a decacarbonyl formulation) but was implied by syntheses of (1) and (2) from $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{10}(NCMe)_2]$, respectively

† *Non-S.I. unit employed:* 1 atm = 101 325 Pa.
‡ *Note added in proof:* The authors have since observed, however, that $[Os_3(CO)_{12}]$ reacts with $[N(PPh_3)_2][N_3]$ in thf at 20 °C.

{using [Au(PEt$_3$)(NCO)]}, and confirmed by a ^{13}C n.m.r. study of ^{13}C-enriched samples. These results are discussed in a preliminary communication.[16] The ^{13}C n.m.r. results indicate that (1) and (2) have the structures shown in the Figure. Thus two functionalized mixed metal clusters can be synthesised in one step and in high yields from [Os$_3$(CO)$_{12}$]. The triphenylphosphine analogues [Os$_3$(CO)$_{11}${Au(PPh$_3$)}(NCO)] (3) and [Os$_3$(CO)$_{10}${Au(PPh$_3$)}(NCO)] (4) can be prepared similarly from [Au(PPh$_3$)Cl].

The reaction of nitrite anions with metal carbonyls has been reported[17] to give anionic nitrosyl complexes. An attempt was made to extend the method employed here for isocyanatogoldtriosmium syntheses into the analogous nitrosyl systems by using nitrite in place of azide anions; this resulted in a 7% yield of [Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NO)] (5)



Scheme 2. Synthesis of [Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NO)] (5)

(Scheme 2). The analogous hydridonitrosyls [Os$_3$(CO)$_{10}$(μ-H)(NO)] and [Ru$_3$(CO)$_{10}$(μ-H)(NO)] are known.[18]

It has been reported[14] that [Os$_3$(CO)$_{10}$(μ-H)(NCO)] undergoes addition reactions with alcohols, amines and hydrazines. Similarly water, methanol, phenylmethanamine and methyl 2-amino-3-phenylpropionate add to [Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NCO)] (2) at 20 °C as shown in Scheme 3. Conditions and yields for these and subsequent reactions are shown in Table 1; the products were characterized by analytical (Table 2), mass spectral, ^{1}H n.m.r., and solution i.r. (Table 3), and solid state i.r. (Table 4) data. The methyl 2-amino-3-phenylpropionate adduct (9) was formed by using only a slight excess of the amine; yields could almost certainly be improved by using more amine or longer reaction times, since 46% of the starting material (2) was recovered. The methyl 2-amino-3-phenylpropionate was formed by esterification of (−)-β-phenylalanine; the product (9) was shown to be chiral [22 mg of (9) in CH_2Cl_2 (2 cm^3) gave a slight negative rotation at 20 °C]. Metal isocyanates thus can sometimes be converted into chiral complexes without resolution; clearly this could have ramifications in the study of catalysts for asymmetric induction.

Goldtriosmium clusters react more readily with phosphines than similar homonuclear osmium clusters as shown by the synthesis of [Os$_3$(CO)$_8$(PPh$_3$){Au(PPh$_3$)}(2-NHC$_5$H$_4$N)] at 20 °C from [Os$_3$(CO)$_9$(μ-H)(2-NHC$_5$H$_4$N)], presumably *via* the nonacarbonyl [Os$_3$(CO)$_9${Au(PPh$_3$)}(2-NHC$_5$H$_4$N)] which is also isolated in the reaction.[13] Such enhanced

Table 1. Reactions of [Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NCO)] (2) and [Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NCNPh)] (14) [a]

Starting material	Reagent	Solvent	Time	Product	Yield (%)
(2)	H_2O	thf	5 min	[Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NHCO$_2$H)] (6)	71
(2)	MeOH	MeOH	24 h	[Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NHCO$_2$Me)] (7)	86
(2)	PhCH$_2$NH$_2$	thf	15 min	[Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NHCONHCH$_2$Ph)] (8)	94
(2)	PhCH$_2$CH(CO$_2$Me)NH$_2$	C_6H_6	64 h	[Os$_3$(CO)$_{10}${Au(PEt$_3$)}{NHCONHCH(CO$_2$Me)CH$_2$Ph}] (9)	41
(2)	PPh$_3$	thf	2 h	[Os$_3$(CO)$_9$(PPh$_3$){Au(PEt$_3$)}(NCO)] (10)	66
(2)	PEt$_3$	thf	5 min	[Os$_3$(CO)$_9$(PEt$_3$)$_3$] (12)	77
(2)	BH$_3$·thf	thf	17 h	[Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NHCHO)] (13)	26
(2)	PhNPPh$_3$	MePh	50 min	[Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NCNPh)] (14)	91
(14)	PhCH$_2$NH$_2$	thf	15 min	[Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NHCNPhNHCH$_2$Ph)] (15)	99
(14)	BH$_3$·thf	thf	1 h	[Os$_3$(CO)$_{10}${Au(PEt$_3$)}(NHCHNPh)] (16)	26

[a] All reactions at 20 °C except the formation of (10) (at 65 °C).

Table 2. Analytical data [a]

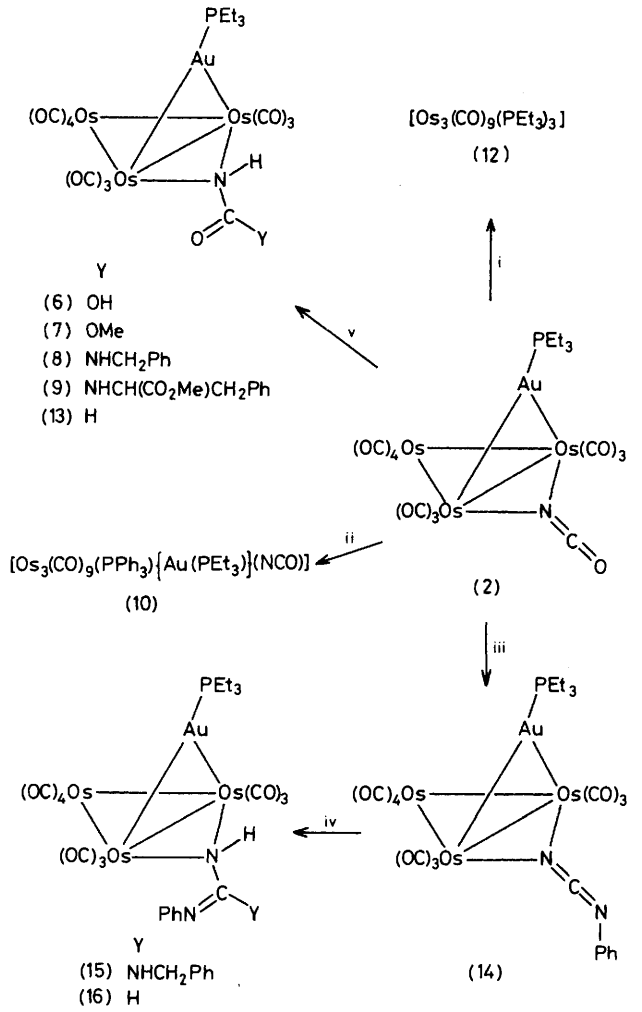
	Found (%)				Required (%)		
Compound	C	H	N	Formula	C	H	N
(1)	17.55	1.25	1.1	$C_{18}H_{15}AuNO_{12}Os_3P$	17.5	1.2	1.1
(2)	16.8	1.25	1.15	$C_{17}H_{15}AuNO_{11}Os_3P$	16.9	1.25	1.15
(3)	26.3	1.15	0.90	$C_{30}H_{15}AuNO_{12}Os_3P$	26.1	1.1	1.0
(4)	26.0	1.15	1.05	$C_{29}H_{15}AuNO_{11}Os_3P$	25.75	1.1	1.05
(5)	16.0	1.3	1.35	$C_{16}H_{15}AuNO_{11}Os_3P$	16.05	1.25	1.15
(6)	16.35	1.3	1.05	$C_{17}H_{17}AuNO_{12}Os_3P$	16.65	1.4	1.15
(7)	17.45	1.55	1.2	$C_{18}H_{19}AuNO_{12}Os_3P$	17.45	1.55	1.15
(8)	21.7	1.8	2.1	$C_{24}H_{24}AuN_2O_{11}Os_3P$	21.9	1.85	2.1
(9)	23.6	2.1	2.1	$C_{27}H_{28}AuN_2O_{13}Os_3P$	23.85	2.05	2.05
(10)	29.2 [b]	2.05	1.0	$C_{34}H_{30}AuNO_{10}Os_3P_2$	28.3	2.1	0.95
(11)	34.75	1.75	1.0	$C_{47}H_{30}AuNO_{11}Os_3P_2$	34.95	1.85	0.85
(12)	27.45	3.8		$C_{27}H_{45}O_9Os_3P_3$	27.55	3.8	
(13)	16.85	1.4	1.1	$C_{17}H_{17}AuNO_{11}Os_3P$	16.9	1.4	1.15
(14)	21.45	1.55	2.15	$C_{23}H_{26}AuN_2O_{10}Os_3P$	21.55	1.55	2.2
(15)	25.75	2.05	2.85	$C_{30}H_{27}AuN_3O_{10}Os_3P$	25.95	1.95	3.05
(16)	21.2	1.75	2.1	$C_{23}H_{22}AuN_2O_{10}Os_3P$	21.5	1.75	2.2

[a] Cambridge University microanalytical department. [b] Trace impurity detected in solution.

Table 3. Spectral data for the complexes (1)—(16)

Compound	*m/z* (*M*, ^{192}Os)	^1H N.m.r. (δ) Solvent	C_6H_5 (m)	NH (br, s)	PCH_2CH_3 (m)	Other	ν_{CO}/cm^{-1} (hexane)
(1)	1 213 [a]	$CDCl_3$			2.53—1.92 (6 H) 1.56—0.96 (9 H)		2 250s,[b] 2 107m, 2 077m, 2 070m, 2 052s, 2 037s, 2 030s, 2 017m, 2 007m, 1 975m, 1 963w, 1 943w
(2)	1 213	$CDCl_3$			2.15—1.73 (6 H) 1.41—0.99 (9 H)		2 300s,[b] 2 093m, 2 046s, 2 041 (sh), 2 012 (sh), 2 008s, 1 989w, 1 981m, 1 967m
(3)	*c*	CD_2Cl_2	7.69—7.46				2 232m,[b] 2 107s, 2 072w, 2 056s, 2 041s, 2 034s, 2 022m, 2 010m, 1 987m, 1 964w
(4)	*c*	CD_2Cl_2	7.65—7.46				2 222m,[b] 2 093m, 2 048s, 2 042 (sh), 2 012 (sh), 2 009s, 1 990w, 1 982m, 1 969w
(5)	1 201	$CDCl_3$			2.06—1.89 (6 H) 1.56—1.06 (9 H)		2 092m, 2 046s, 2 017s, 2 008s, 1 990 (sh), 1 986m, 1 978m
(6)	1 231	$CDCl_3$		5.09 (1 H)	2.00—1.79 (6 H) 1.39—1.06 (9 H)	2.2 (br, 1 H)	2 088w, 2 043s, 2 036 (sh), 2 006m, 1 989m, 1 972m [d]
(7)	1 245	$CHCl_3$		5.16 (1 H)	1.98—1.72 (6 H) 1.48—1.01 (9 H)	3.71 (s, 3 H)	2 088w, 2 044s, 2 036m, 2 009m, 1 991s, 1 965 [d]
(8)	1 320	CD_2Cl_2	7.32 (5 H)	5.06 (1 H) 1.50 (2 H)	2.10—1.69 (6 H) 1.38—0.96 (9 H)	4.37 (d, J = 6, 2 H)	2 082w, 2 036s, 2 032 (sh), 2 002m, 1 974m, 1 966m
(9)	1 392	CD_2Cl_2	7.38—7.08 (5 H)	5.27 (1 H) 1.50 (2 H)	2.12—1.80 (6 H) 1.39—1.13 (9 H)	4.72—4.53 (m, 1 H) 3.70 (s, 3 H) 3.12 (d, J = 6, 2 H)	2 083w, 2 039s, 2 031 (sh), 2 003w, 1 994w, 1 981m, 1 968m
(10)	1 447	CD_2Cl_2	7.60—7.21 (15 H)		1.63—1.27 (6 H) 1.18—0.75 (9 H)		2 350s,[b] 2 078m, 2 032s, 2 002 (sh), 1 996m, 1 981m, 1 970w, 1 960w, 1 949w
(11)	*c*	CD_2Cl_2	7.61—7.03				2 339s,[b] 2 079m, 2 036s, 2 003 (sh), 1 999s, 1 985w, 1 973w, 1 955w, 1 930w
(12)	1 182	$CDCl_3$			2.23—1.83 (6 H) 1.33—0.84 (9 H)		1 984 (sh), 1 974s, 1 929m, 1 918m
(13)	1 215	$CDCl_3$		5.2 (1 H)	2.13—1.80 (6 H) 1.55—1.06 (9 H)	7.10 (d, J = 5, 1 H)	2 089m, 2 042s, 2 034s, 2 009m, 1 996s, 1 986m, 1 969m, 1 960m
(14)	1 288	CD_2Cl_2	7.31—7.01 (5 H)		2.10—1.78 (6 H) 1.48—1.01 (9 H)		2 121m,[e] 2 085s, 2 043s, 2 036 (sh), 2 013 (sh), 2 005s, 1 987m, 1 975m, 1 964m
(15)	1 395	CD_2Cl_2	7.37—6.95 (10 H)	5.41 (2 H)	2.13—1.72 (6 H) 1.48—0.98 (9 H)	4.11 (s, 2 H)	2 082m, 2 042s, 2 028s, 1 997m, 1 994s, 1 969w, 1 960 (sh), 1 955m, 1 950m
(16)	1 290	CD_2Cl_2	7.41—6.89 (5 H)	5.4 (1 H)	2.19—1.79 (6 H) 1.52—1.05 (9 H)	6.16 (d, J = 5, 1 H)	2 083m, 2 035 (sh), 2 032s, 1 997s, 1 977w, 1 955m

[a] $M^+ - 28$. [b] NCO str. [c] No molecular ion. [d] In CH_2Cl_2 solution. [e] NCN str.



Scheme 3. Reactions of co-ordinated isocyanates and carbodi-imides. Reagents: i, PEt_3 (excess); ii, PPh_3; iii, $PhNPPh_3$; iv, BH_3·thf for (16), $PhCH_2NH_2$ for (15); v, HY for (6)—(9), BH_3·thf for (13)

reactivity could be a consequence of the gold–osmium bond polarity. The decacarbonyl isocyanates (2) and (4) react with a slight excess of triphenylphosphine to give $[Os_3(CO)_9(PPh_3)\{Au(PR_3)\}(NCO)]$ (10) (R = Et) and (11) (R = Ph). With an excess of triethylphosphine at 20 °C, however, the gold and isocyanate functions were removed from $[Os_3(CO)_{10}\{Au(PEt_3)\}(NCO)]$ (2), and $[Os_3(CO)_9(PEt_3)_3]$ (12) was formed in high yield.

The isocyanate (2) resists hydrogenation (70 atm, in heptane) up to 150 °C, at which temperature the isocyanate absorption disappears but a complex mixture of products is formed (high pressure i.r. apparatus).[18] Reduction of (2) with borane–tetrahydrofuran adduct (BH_3·thf), however, proceeds at 20 °C, affording a formamido cluster $[Os_3(CO)_{10}\{Au(PPh_3)\}(NHCHO)]$ (Scheme 3). Thus a carbonyl ligand can be removed from $[Os_3(CO)_{12}]$ and reduced to a formamide group in two steps *via* a mixed metal isocyanate.

Phosphonium ylides have been shown to react with organic isocyanates;[19] similarly, methylenetriphenylphosphorane reacts with the isocyanate (2) at 20 °C to give a complex mixture of products (not characterized), but phenyliminotriphenylphosphorane ($PhNPPh_3$) reacts cleanly; the isocyanate is thus transformed into an unusual terminally bonded

Table 4. Solid-state i.r. data (ν/cm^{-1}, CsI disc) for some of the complexes

Compound	NH str.	C=O str.	Other
(5)			1 508m (NO str.)
(6)	3 380w	1 700m	*ca.* 2 480 to *ca.* 3 200br, w (O–H)
(7)	3 380w	1 758s	1 180s (C–O str.) [a]
(8)	3 455m, 3 380w	1 708s	
(9)	3 440w, 3 350w	1 710m [b]	1 080s (C–O str.) [a]
(13)	3 335w	1 710s	
(15)	3 410m		1 650s (C=N str.)
(16)	3 400m		1 660s (C=N str.)

[a] Tentative assignment. [b] Slightly broad; seems to be coincident ester and urea carbonyls with the former presumably lowered by intramolecular H-bonding.

carbodi-imide ligand (Scheme 3) to give $[Os_3(CO)_{10}\{Au(PEt_3)\}(NCNPh)]$ (14). The isocyanate (2) and $[Os_3(CO)_{10}\{Au(PEt_3)\}(NCNPh)]$ (14) are structurally similar; their solution i.r. spectra are comparable except for the absence of an isocyanate stretch in (14) and the appearance of a band at 2 121 cm^{-1} attributed to the N=C=N stretch. Consequently an alternative structure in which both nitrogens co-ordinate is disfavoured.

The carbodi-imide (14) is less reactive than the isocyanate (2); it is unchanged after 2 h in methanol at 64 °C. However, addition of benzylamine does occur at 20 °C to give $[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCNPhNHCH_2Ph)]$ (15) (Scheme 3). Only one of the three possible tautomers is shown in Scheme 3; the other two are related by migration of either of the two N–H protons to the C=N bond, and it is not possible to decide from the spectral data which of these, if any, predominates.

Like the isocyanate (2), the carbodi-imide (14) in heptane is inert to 70 atm of hydrogen up to 180 °C, but was chemically reduced by BH_3·thf at 20 °C to give $[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCHNPh)]$ (16) (or its tautomer).

Experimental

Tetrahydrofuran (thf) was distilled from sodium–benzophenone under dinitrogen immediately before use. Reactions were performed under dinitrogen but thin-layer chromatography (t.l.c.) was performed in air using commercial Merck silica plates. Mass spectra were recorded on an A.E.I. MS 12 spectrometer, i.r. spectra on a Perkin-Elmer 257, ^{1}H n.m.r. spectra on a Varian CFT 20 at 80 MHz, and ^{13}C n.m.r. spectra on a Brucker WM spectrometer at 250 MHz. All samples were recrystallized from hexane or hexane–dichloromethane at −30 °C.

Isocyanate Clusters (1)—(4).—(*i*) *From* $[Os_3(CO)_{12}]$. Equimolar quantities of $[Os_3(CO)_{12}]$ (*ca.* 100 mg), 18-crown-6, $[Au(PEt_3)Cl]$, and sodium azide were stirred in thf (20 cm^3) at 20 °C for 15 h. The mixture was filtered (Celite), the solvent removed, and the residue subjected to t.l.c. (50% dichloromethane–hexane eluant) to give (1) and (2) as a yellow and a red band, respectively. When this procedure was repeated but with a reaction temperature of 65 °C for 4 h, only cluster (2) was isolated.

(*ii*) *From* $[Os_3(CO)_{11}(NCMe)]$. $[Os_3(CO)_{11}(NCMe)]$ (28 mg) and $[Au(PEt_3)(NCO)]$ (1 mol equiv.) were stirred in benzene (5 cm^3) at 20 °C for 1 h. Removal of the solvent and t.l.c. (dichloromethane eluant) gave (1) (31%) and (2) (26%).

(*iii*) *From* $[Os_3(CO)_{10}(NCMe)_2]$. The complex (2) was isolated in 75% yield by using procedure (*ii*) but with a 16 h reaction time.

The complex (1) showed δ_C (CD_2Cl_2; −80 °C) 191.0 (s), 190.9 (s), 187.6 (s), 187.5 (s), 186.9 (s), 184.6 (s), 182.5 (s), 180.3 (s), 178.0 (s), 176.3 (s), 176.2 (s), 175.9 (s), 175.5 (s), 175.3 (s), 174.8 (s), 173.9 (s), 170.4 (s), and 170.2 (s) (1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 : 2 : 1 : 1 : 2 : 1 : 1 : 2 : 2 : 1 : 1 pattern), 129.3 (s), 125.5 (s), 18.5 (d, J = 17 Hz), 9.2 (s). The complex (2) showed δ_C 186.0 (s), 184.1 (s), 182.3 (s), 180.5 (s), 178.9 (s), 175.3 (s), and 175.2 (s) (1 : 1 : 2 : 2 : 2 : 1 : 1 pattern), 134.6 (s), 19.7 (d, J = 17, Hz), and 8.9 (s). The triphenylphosphine analogues (3) and (4) can be prepared by procedure (*i*), (*ii*), or (*iii*) in an analogous way.

$[Os_3(CO)_{10}\{Au(PEt_3)\}(NO)]$ (5).—$[Os_3(CO)_{12}]$ (103 mg), $[Au(PEt_3)Cl]$ (1.1 mol equiv.), 18-crown-6 (*ca.* 6 mg), and sodium nitrite (30 mol equiv.) were stirred in thf (10 cm^3) at 20 °C for 64 h. Removal of the solvent and t.l.c. (35% dichloromethane–hexane) gave (5) as a green band.

$[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCO_2H)]$ (6).—Isocyanate (2) (84 mg) and water (0.1 cm^3) were stirred in thf (10 cm^3) for 5 min. Removal of the solvent and t.l.c. (50% acetone–hexane) gave (6) as an orange band.

$[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCO_2Me)]$ (7).—$[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCONHCH_2Ph)]$ (8) and $[Os_3(CO)_{10}\{Au(PEt_3)\}\{NHCONHCH(CO_2Me)CH_2Ph\}]$ (9) were prepared in a similar way to (6) but with the reaction conditions specified in Table 1 and 50% dichloromethane–hexane as t.l.c. eluant [5 mol equiv. of methyl 2-amino-3-phenylpropionate were used for (9)].

$[Os_3(CO)_9(PPh_3)\{Au(PEt_3)\}(NCO)]$ (10).—Isocyanate (2) (46 mg) and triphenylphosphine (1.2 mol equiv.) were maintained in refluxing thf (10 cm^3) for 2 h. Removal of the solvent and t.l.c. (40% dichloromethane–hexane) gave (10) as a purple band. The phenyl analogue (11) was prepared by the same procedure from (4).

$[Os_3(CO)_9(PEt_3)_3]$ (12).—Isocyanate (2) (47 mg) and triethylphosphine (0.5 cm^3) were stirred in dry thf (10 cm^3) for 5 min. Removal of the solvent and t.l.c. (40% dichloromethane–hexane) gave (12) as an orange band.

$[Os_3(CO)_{10}\{Au(PEt_3)\}(NCNPh)]$ (14).—Isocyanate (2) (100 mg) was treated with phenyliminotriphenylphosphorane (1.0 mol equiv.) at 20 °C in methylbenzene (10 cm^3) for 50 min. Removal of the solvent and t.l.c. (40% dichloromethane–hexane) gave (12) as an orange band.

$[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCHO)]$ (13) *and* $[Os_3(CO)_{10}\{Au(PEt_3)\}\{NHCHNPh)]$ (16).—Clusters (2) and (14) were each stirred with BH_3·thf (0.4 cm^3 of a 1 mol dm^{-3} solution in thf) under the conditions indicated in Table 1. Removal of the solvent and t.l.c. (45% dichloromethane–hexane) gave the clusters as yellow (13) and orange (16) bands.

$[Os_3(CO)_{10}\{Au(PEt_3)\}(NHCNPhNHCH_2Ph)]$ (15).—The carbodi-imide cluster (14) (81 mg) and benzylamine (0.2 cm^3) were stirred in thf (5 cm^3) at 20 °C for 15 min. Removal of the solvent and t.l.c. (14% ethyl acetate–hexane) gave (15) as a yellow band.

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Received 10*th September* 1982; *Paper* 2/1557