PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Phil. Trans. R. Soc. Lond. A 1982 **308**, 59-66
doi: 10.1098/rsta.1982.0146

Phil. Trans. R. Soc. Lond. A **308**, 59–66 (1982)
Printed in Great Britain

Nucleophilic addition at μ_3-alkyne clusters leading to carbon–carbon bond formation

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Reactions of nucleophiles with triosmium carbonyl clusters, especially those containing unsaturated hydrocarbon ligands, are discussed. Attack may be at CO, the metal atoms, at carbon of the organic ligand, or, where there are acidic metal-bound hydrogen atoms, deprotonation to give anionic clusters may occur.

New results on the reactions of $LiBHEt_3$ with μ_3-alkyne clusters of type $Os_3(CO)_{10}(RC_2R')$ are considered in the light of the range of possible sites of attack. Protonation of anionic species that are formed gives hydrogenation products with or without the loss of CO. $Os_3H_2(CO)_9(RC_2R')$ is usually a minor product, while C–C coupling leads to $Os_3H(CO)_9(CRCR'COH)$ (in general the major product) and to $Os_3H(CO)_9(CRCR'CH)$. With terminal alkynes RC_2H H-atom transfer accompanies C–C coupling to give $Os_3H(CO)_9(RC{=}C{=}CH_2)$ in substantial amounts. The initial site of hydride attack (CO, alkyne or metal) is considered in the context of low-temperature ^1H n.m.r. results.

Introduction

Clusters have modes of reactivity that are unavailable to mononuclear compounds and in addition to those found for mononuclear species. Reaction steps may involve a modification of the metal–metal bonds; changes in order of these bonds or in the geometry of the metal framework are found. Changes in nuclearity are a direct extension of this. Furthermore, certain reaction types are expected to relate to the presence and unique character of bridging ligands. There have been few mechanistic studies on known reactions of clusters, while for the most part we are still at the stage of defining reactions of clusters. Odd-electron processes (radical and redox reactions) may prove in time to be of great importance in cluster chemistry, but most reactions so far identified may be thought of as even-electron processes involving electrophilic and nucleophilic centres, either or both of which may be at the cluster.

It is remarkable how much of our present knowledge of clusters is based on the very simple clusters, $M_3(CO)_{12}$ (M = Fe, Ru, or Os) and trinuclear derivatives of these (see, for example, Johnson 1980). Triosmium compounds are particularly inert and tractable, and their reactions most readily studied. We shall concentrate on these exclusively.

Most carbonyl triosmium clusters are attacked by electrophiles (H^+ in particular) at the metal atoms to give bridging metal hydrides or sometimes at the oxygen atoms of CO ligands (Gavens & Mays 1978). Perhaps attack at oxygen precedes subsequent intramolecular transfer of the electrophile (H^+) to the metal atoms even in cases where the final product is the metal hydride. Protonation at a carbon atom of organic ligands is rare. One case we have observed recently is the protonation of the vinyloxy-ligand in $Os_3H(CO)_{10}(\mu\text{-}OCH{=}CH_2)$ by trifluoroacetic acid in $CDCl_3$ at -50 °C to give the ethanal compound $[Os_3H(CO)_{10}(CH_3CHO)][CF_3CO_2]$, which readily converts to $Os_3H(CO)_{10}(CF_3CO_2)$ with the liberation of free ethanal on warming to room temperature (A. J. Arce, A. J. Deeming & J. Watson-Miller, unpublished 1982).

We shall begin with a survey of the attack of nucleophiles at trimetallic clusters, giving examples in the main from our own recent work. The second part of this paper is a description of the addition of hydride ions (as $LiBHEt_3$) to alkyne complexes of the type $Os_3(CO)_{10}$(alkyne) leading to C–C bond formation at the alkynes and other reactions.

NUCLEOPHILIC ADDITION AT TRIOSMIUM CLUSTERS

(*a*) *Attack at* CO

This occurs commonly where there are no organic ligands present that are more electrophilic than CO. $Os_3(CO)_{12}$ reacts with amines RNH_2 to give $Os_3H(CO)_{10}(RNHCO)$ (**1**), containing the amido ligand bridging two osmium atoms; the reaction occurs readily at room temperature if the neat amine is used (Kaesz *et al.* 1982; Azam *et al.* 1978; Arce & Deeming 1980). An initial equilibrium is set up between $Os_3(CO)_{12}$ and $[RNH_3][Os_3(CO)_{11}(RNHCO)]$, but the rather easy loss of CO leading to **1** is an irreversible step. Spectroscopic and X-ray crystallographic studies on the Ru analogue have confirmed the structure shown for **1** rather than isomeric forms that are also known. The oxidative decarbonylation of carbonyl clusters by using Me_3NO is similarly irreversible. We believe that this type of reaction occurs extremely generally and may be an unidentified first step in many known reactions with nucleophiles or is not normally observed because of ready reversibility. For example, the 2-pyridyl compound $Os_3H(CO)_{10}(NC_5H_4)$ (**2**) (Choo Yin & Deeming 1975) dissolves in undiluted benzylamine to give a new hydrido-species in solution with ν(CO) absorptions just over 30 cm^{-1} lower than

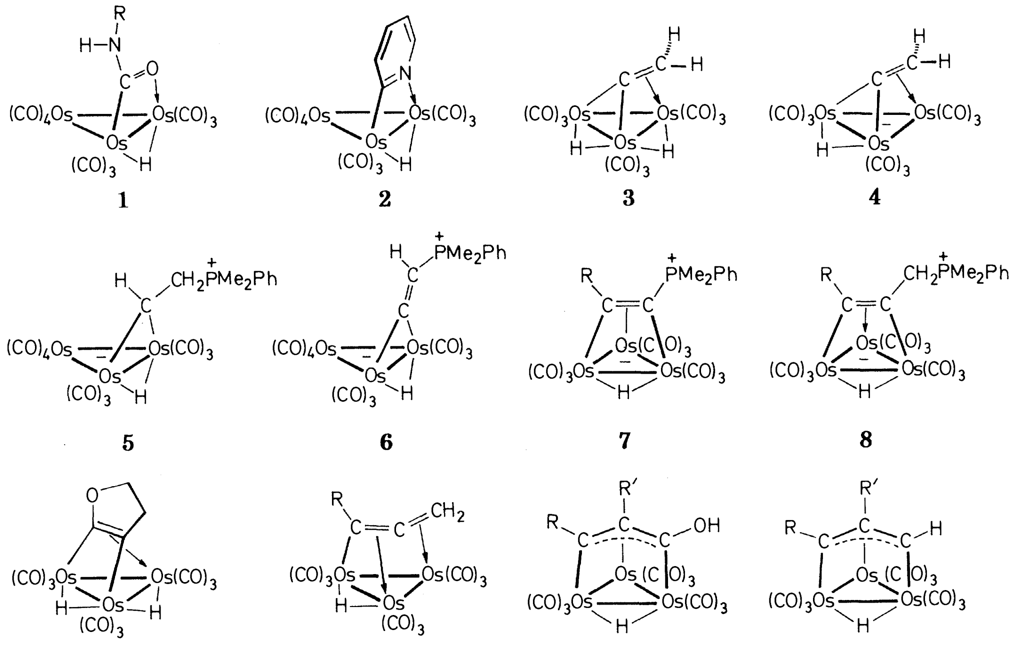

FIGURE 1. Structures of triosmium compounds numbered in the text.

for **2**. Addition of small amounts of chloroform to this solution regenerates **2** totally. Corresponding changes are observed in the ^1H n.m.r. spectrum and we believe that the species formed is $[RNH_3][Os_3H(CO)_9(NC_5H_4)(RNHCO)]$ (A. J. Arce, A. J. Deeming & R. Shaunak, unpublished 1982). We do not know why the anionic RNHCO species does not lose CO with irreversible product formation in this case, while the loss of CO occurs so readily when $Os_3(CO)_{12}$ or $Ru_3(CO)_{12}$ are dissolved in the undiluted amine.

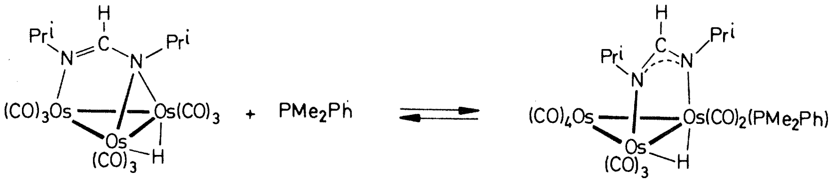

FIGURE 2. Reversible uptake of PMe_2Ph facilitated by a change in the bonding of the $Pr^iNCHNPr^i$ ligand to the triosmium cluster.

(*b*) *Attack at metal*

Although direct nucleophilic attack at metal atoms in normal oxidation states is typical behaviour, metal compounds in a low oxidation state usually require special features for such reaction. Essentially all the reactions of $Os_3H_2(CO)_{10}$ may be regarded as going via a direct nucleophilic addition at metal (Shapley *et al.* 1975; Deeming & Hasso 1975*a*, 1976*a*). For example, it has been shown recently that many anions, including halide, add to this dihydride directly (Kennedy *et al.* 1981). The compound may not contain a double metal–metal bond but certainly reacts as an unsaturated molecule. Another formally unsaturated species that undergoes additions is $Os_3(CO)_9(PhC_2Ph)$ (Clauss *et al.* 1981), while clusters with weakly bound ligands L such as $Os_3(CO)_{10}L_2$ (L = acetonitrile, for example) presumably undergo reversible loss of L to give reactive unsaturated species. In other cases direct addition at the metal is possible because a ligand already present transforms from an n to an $n-2$ electron donor. In known examples it is not clear whether the modification occurs unimolecularly before nucleophilic addition at the metal or whether the nucleophilic attack induces the transformation. Figure 2 illustrates an example of this behaviour (Deeming & Peters 1982), and similar interconversions also occur with the corresponding compound from 2-aminopyridine (Deeming *et al.* 1982).

Modification of the metal skeleton of the cluster to allow direct nucleophilic attack, although uncommon for triosmium species, becomes a feature of higher clusters. There are a few cases of the transfer of a nucleophile from an organic ligand to the metal. The alkynyl cluster $Os_3H(CO)_9(C{\equiv}CCPh_2OH)$ undergoes an acid-catalysed isomerization to $Os_3H(OH)(CO)_9(C{=}C{=}CPh_2)$ and it is likely that the unsaturated intermediate $[Os_3H(CO)_9(C{=}C{=}CPh_2)]^+$ is attacked at the metal directly by OH^- or H_2O. Nucleophilic attack leads to an opening of one edge of the metal triangle (Aime *et al.* 1982).

(*c*) *Deprotonation*

Many triosmium carbonyl clusters contain metal-bound hydrogen atoms that generally show protic rather than hydridic character. Thus nucleophiles, especially good bases, often deprotonate clusters. The vinylidene complex $Os_3H_2(CO)_9(C{=}CH_2)$ (**3**) is readily deprotonated to give the anion (**4**), which may be isolated as $[N(PPh_3)_2][Os_3H(CO)_9(C{=}CH_2)]$. The equivalence of the vinylidene hydrogen atoms shows that deprotonation generates a plane of symmetry. Deprotonation occurs in spite of the vinylidene ligand's being a potential electrophilic centre even with cyanide ion, which is a good nucleophile towards carbon in most cases.

(*d*) *Attack at organic ligands*

Nucleophilic attack commonly occurs at η-alkene (monoene or polyene) in cationic complexes, not so much because of electron withdrawal from the alkene by the metal but because of transition state stabilization caused by a formation of a σ-metal–carbon bond (in the monoene) synchronous with the formation of a bond from carbon to the nucleophile. The ability of the alkene to slide across the metal is important in this respect (Eisenstein & Hoffmann 1981). Neutral metal clusters are attacked, as in the addition of PMe_2Ph to $Os_3H(CO)_{10}(CH{=}CH_2)$ to give **5** (Deeming & Hasso 1976*b*; Churchill *et al.* 1976). As well as PMe_2Ph, other nucleophiles such as RO^-, $NHEt_2$, ArS^-, and CN^- also add. The alkyne cluster $Os_3(CO)_{10}(C_2H_2)$ gives the PMe_2Ph adduct (**6**), $Os_3H(CO)_9(C{\equiv}CR)$ gives **7**, and $Os_3H(CO)_9(CR{=}C{=}CH_2)$ gives **8**. The X-ray structures of **6**, **7** (R = H) and **8** (R = Me) have been determined (Henrick *et al.* 1982). In contrast, other alkyne clusters of the type $Os_3(CO)_{10}$(alkyne) do not add PMe_2Ph, other than by slow reaction to give substitution compounds. Only with C_2H_2 can PMe_2Ph attack at a CH terminus, allowing a hydrogen atom to be transferred then from the other carbon of the alkyne. Presumably the initial attack without a subsequent H-atom transfer is unfavourable. The allyl complexes $Os_3H(CO)_9(CRCR'CR'')$ are also unreactive towards PMe_2Ph at room temperature.

Of the examples we have studied, the α-carbon of the alkynyl complexes $Os_3H(CO)_9(C{\equiv}CR)$ appears the most electrophilic, and c.n.d.o. calculations indicate that this carbon carries more positive charge than the adjacent one but less than the carbonyl carbon atoms (Granozzi *et al.* 1982). The hydroxy-alkyne $HC{\equiv}CCH_2CH_2OH$ reacts with $Os_3(CO)_{12}$ to give the dihydrofuran derivative, **9**. The same compound is obtained from $Os_3(CO)_{10}(MeCN)_2$ via $Os_3(CO)_{10}(HC_2CH_2CH_2OH)$ and $Os_3H(CO)_9(C{\equiv}CCH_2CH_2OH)$. The latter compound undergoes an intramolecular nucleophilic attack at the α-carbon atom to give **9** (S. Aime & A. J. Deeming, unpublished 1982).

HYDRIDE ION ATTACK AT $Os_3(CO)_{10}$(alkyne)

Of the complexes of the type $Os_3(CO)_{10}$(alkyne) only the C_2H_2 complex is readily attacked by PMe_2Ph (see above). The monosubstituted and disubstituted alkyne compounds show no rapid reaction with PMe_2Ph to give zwitterionic adducts, only slowly giving $Os_3(CO)_{10}(PMe_2Ph)_2$. Hydride ions (as $LiBHEt_3$) react rapidly with all the compounds of this type that we have studied, to give, after acidification and chromatographic separation, various products (**10**, **11** and **12**) (figure 1) and $Os_3H_2(CO)_9$(alkyne) (**13**). Yields and spectroscopic data are given in table 1. A few of these clusters are new, but all are of known types and were easily characterized by comparing their spectroscopic data with those reported. Notably, except for **13**, which is formed in low yield in most reactions, all these compounds result from the reduction of a CO ligand and its coupling to the alkyne ligand. The hydroxyallyl compounds (**11**) were previously formed by reacting $Os_3(CO)_{11}(MeCN)$ with the alkyne RC_2H (R = H, Me or Ph) in moist CH_2Cl_2 but not with disubstituted alkynes (Hanson *et al.* 1980). By our route, compounds **11** were synthesized from but-2-yne and diphenylacetylene (R = R′ = Me or Ph). The

TABLE 1. YIELDS AND SPECTROSCOPIC DATA FOR PRODUCTS FROM TREATING $Os_3(CO)_{10}$(ALKYNE) WITH $LiBHEt_3$

alkyne	products	yield (%)	ν(CO)/cm^{-1}†					selected ^{1}H n.m.r. data; δ‡
HC_2H	$Os_3H^w(CO)_9(CH^x{=}C{=}CH_2^{y,z})$	2	2101m 2003s	2072vs 1994m	2047vs 1986w	2026vs 1982mw	2017s	9.11d (H^x) (J = 1.9 Hz), 4.30s, 2.61s (H^yH^z), −22.43d (H^w)
	$Os_3H(CO)_9(CHCHCOH)$	68§						
	$Os_3H(CO)_9(CHCHCH)$	3	2100 2004s	2072s 1990w	2051s 1979w	2021s	2010m	
	$Os_3H_2(CO)_9(HC_2H)$	5	2110m 2013s	2082s 2004m	2058s 1991sh	2033s 1986m	2026m	8.63d (C_2H_2) (J = 1.3 Hz), −21.62††, −18.50d (J = 1.0 Hz)
MeC_2H	$Os_3H(CO)_9(MeC{=}C{=}CH_2)$	43	‖					
	$Os_3H^x(CO)_9(CH^yCMeCOH)$¶	16	2098m 2046sh 2001sh	2096sh 2022vs 1998vs	2068vs 2018sh 1995sh	2066sh 2012m 1990sh	2049vs 2007s	2.89s (Me), 7.67d (H^y) (J = 1.5 Hz), −18.80d (H^x)
	$Os_3H(CO)_9(MeCCHCH)$	9	‖					
	$Os_3H_2(CO)_9(MeC_2H)$	7	2110m 2012vs	2081vs 2003s	2058vs 1985s	2033vs	2026s	8.03s (CH), 2.81s (Me), −17.97s, −21.49s
PhC_2H	$Os_3H^x(CO)_9(PhC{=}C{=}CH_2^{y,z})$	25	2100s 2003s	2072vs 1993m	2048vs 1987w	2026vs 1982m	2019s	4.14d (H^y), 2.65d (H^z) (J = 2 Hz), −22.34s (H^x)
MeC_2Me	$Os_3H(CO)_9(CMeCMeCOH)$	22	2095m 2003s	2068sh 1996vs	2065vs 1986sh	2046vs 1957vw	2014vs	2.12s (Me), 2.93s (Me), −18.69s (OsH)
	$Os_3H^x(CO)_9(CMeCMeCH^y)$	7	2099w 2002s	2070vs 1990w	2048vs	2020s	2008m	2.86s (Me), 2.51s (Me), 8.78s (H^y), −19.23s (H^x)
	$Os_3H_2(CO)_9(MeC_2Me)$	26	2106w 2009vs	2080vs 1997s	2054vs 1981m	2030vs	2020m	2.49s (Me_2), −17.99s (OsH), −21.46s (OsH)‡‡
PhC_2Ph	$Os_3H^x(CO)_9(CPhCPhCOH^y)$	51	2099s 2005vs	2074vs 1988sh	2043vs 1983m	2024vs	2011s	6.4s (H^y) (temp. variable), −18.78s (H^x)
	$Os_3H_2(CO)_9(PhC_2Ph)$‖	trace	2108m 2015vs	2083vs 1999s	2057vs 1995sh	2032vs 1983s	2027vs	−17.30s, −21.21s
	$Os_3H(CO)_9(CPhCPhCH)$	trace						

† In cyclohexane solution. ‡ In $CDCl_3$. § Hanson *et al.* (1980). ‖ Deeming *et al.* (1975). ¶ Isomeric $Os_3H(CO)_9(CMeCHCOH)$ (Hanson *et al.* 1980). †† Apparent quartet; doublet of triplets with equal coupling to the C_2H_2 protons, −17 °C. ‡‡ Coalesced hydride signal at −19.43; T_c 1 °C.

complex from propyne has distinctly different ^1H n.m.r. data from those reported for $Os_3H(CO)_9(MeCCHCOH)$, so our compound may have the opposite regiospecificity, that is $Os_3H(CO)_9(CHCMeCOH)$. These compounds exist as only slowly interconverting isomers, as already described (Hanson *et al.* 1980).

Other products, **10** and **12**, involve further reduction of the coupled CO with the loss of an oxygen atom. These compounds seem to be favoured when rather larger excesses of $LiBHEt_3$ (such as a fivefold excess) are used.

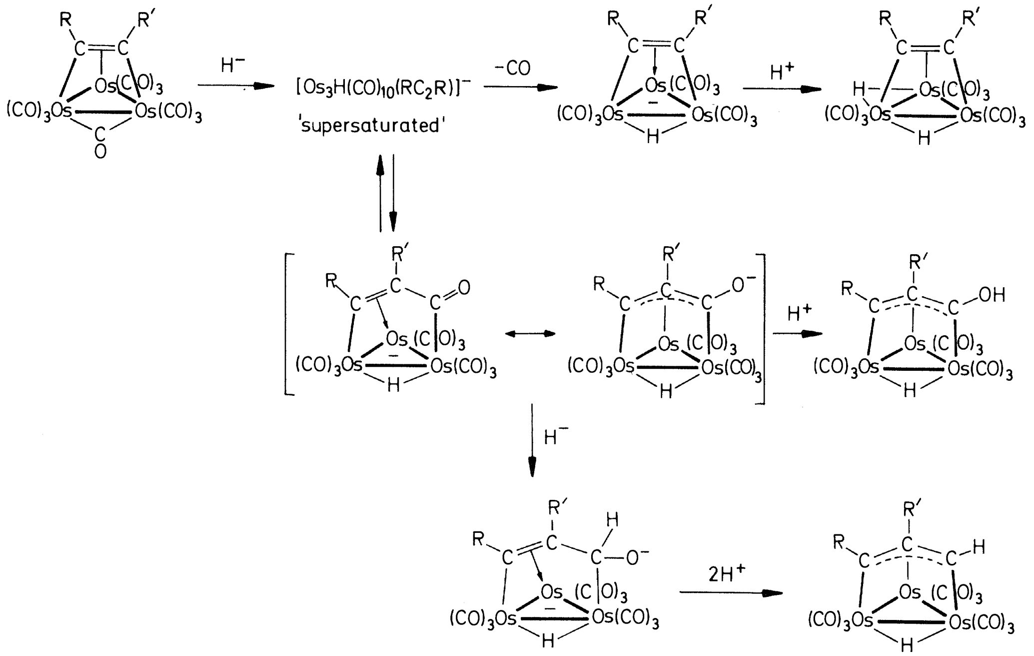

FIGURE 3. A possible reaction pathway resulting from the treatment of $OS_3(CO)_{10}$(alkyne) with $LiBHEt_3$ involving hydride addition at metal atoms. The compound $[Os_3H(CO)_{10}(\text{alkyne})]^-$ is only supersaturated if the alkyne remains as a μ_3-four-electron donor and if there is no Os–Os bond cleavage.

To learn of the origin of compounds **10–13** we studied the addition of $LiBHEt_3$ (twofold excess) in THF to $Os_3(CO)_{10}(C_2H_2)$ in d^8-THF at −20 °C. Rapid changes in the ^1H n.m.r. spectrum were observed. The single C_2H_2 resonance is replaced by ten new signals between $\delta = 6$ and 15, together with two hydride signals. Clearly the system is complicated. One set of signals observed immediately ($\delta = 7.90$d, 6.65d and −18.10s) corresponds to the deprotonated form of the hydroxyallyl, $[Os_3H(CO)_9(CHCHCO)]^-$, and this persists indefinitely at this temperature. The deprotonated form of $Os_3H_2(CO)_9(C_2H_2)$ is only slowly formed at the expense of other signals in the spectrum (spectrum of $[Os_3H(CO)_9(C_2H_2)]^-$, $\delta = 8.60$s and −21.13s). After several hours at −20 °C the spectrum had simplified and the solution contained mainly $[Os_3H(CO)_9(C_2H_2)]^-$ and $[Os_3H(CO)_9(CHCHCO)]^-$, and protonation with CF_3CO_2H gave $Os_3H_2(CO)_9(C_2H_2)$ and $Os_3H(CO)_9(CHCHCOH)$. These were each isolated in approximately 30% yield.

Very weak signals ($\delta = 14.9$ and 13.6) in the early stages of the reaction could be of formyl species but after several hours these had disappeared. The room temperature addition of $LiBHEt_3$ (4 mol per Os_3) also gave $Os_3H(CO)_9(CHCHCH)$ and $Os_3H(CO)_9(CH{=}C{=}CH_2)$ in low yield, but these were not observed in the reaction at −20 °C. Presumably they are formed in secondary reactions.

Two basic but not necessarily exclusive reaction schemes are shown in figures 3 and 4. The route via formyl intermediates in figure 4 is supported by the observation of weak low-field signals, but we believe that the route would not result in C–C coupling until after protonation. The formation of the CHOH and CH_2 complexes is based on the route to $Os_3(CO)_{11}(CH_2)$ by hydride ion attack at $Os_3(CO)_{12}$ (Steinmetz & Geoffroy 1981). The final stages of the scheme in figure 4 require isomerizations with alkyne to CH_2 or CHOH coupling. There is some precedent for this in the isomerization of $Os_3(CO)_9(CH_2)(PhC_2Ph)$ to $Os_3H(CO)_9(CPhCPhCH)$, but this requires a temperature of 135 °C and does not occur at room temperature (Clauss *et al.* 1981). We favour the scheme in figure 3 as the main route. Addition of hydride at the metal atoms, or possibly an initial attack at C_2H_2 or CO followed by H-atom transfer to the metal atoms, would give $[Os_3H(CO)_{10}(C_2H_2)]^-$. This is supersaturated if the alkyne remains a μ_3-four-electron-donor ligand. This could then lose CO or undergo C–C coupling. The latter might be favoured by a four-electron to two-electron donor transformation of the alkyne. Interestingly C_2H_2 reacts with $Os_3(CO)_{11}(CH_3CN)$ with C–C coupling and the presumed intermediate, $Os_3(CO)_{11}(C_2H_2)$ is closely related in electron-counting to $[Os_3H(CO)_{10}(C_2H_2)]^-$. Coupling of CO with alkyne is well known, of course, but not studied mechanistically. The coupling may be rapidly reversible in some cases at least (Dyke *et al.* 1980; Finnimore *et al.* 1980) and the slow formation of $[Os_3H(CO)_9(C_2H_2)]^-$ by CO loss may result from a reversal of C–C coupling.

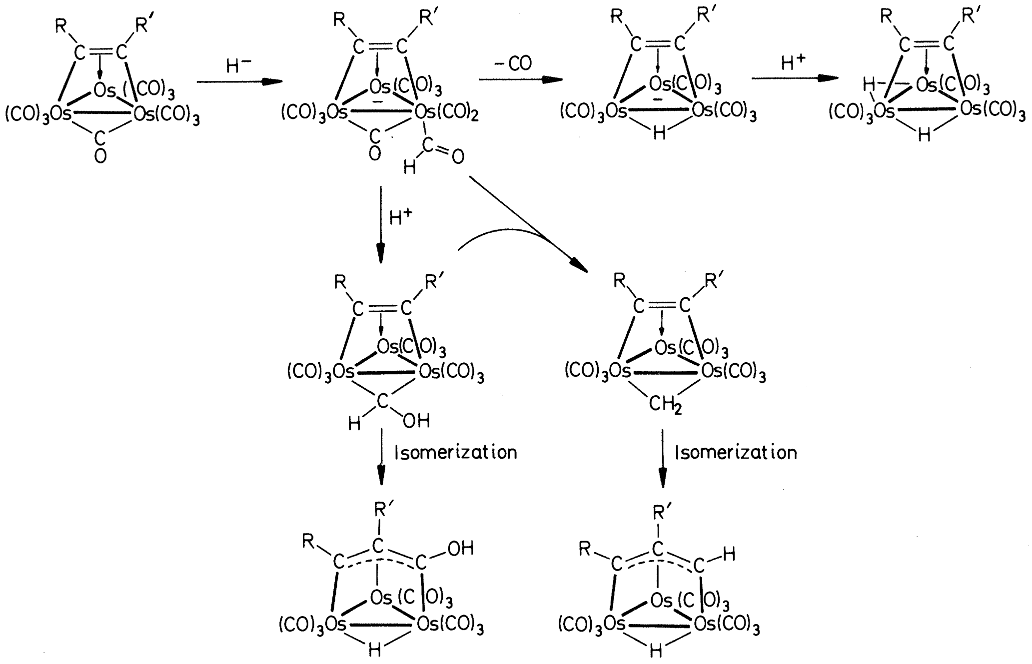

FIGURE 4. An alternative reaction pathway based on hydride addition at CO to give intermediate formyl species.

EXPERIMENTAL

We synthesized the alkyne complexes $Os_3(CO)_{10}$(alkyne) by treating $Os_3(CO)_{10}(MeCN)_2$ with the alkyne. All these alkyne complexes have the structure shown in figures 3 and 4 with bridging carbonyl except for the PhC_2Ph complex, which has only terminal CO in the crystal. In solution, weak absorptions due to bridging CO are observed even for $Os_3(CO)_{10}(PhC_2Ph)$. Between 60 and 270 mg of the alkyne complexes were used for the hydride addition. Yields in table 1 are given for the isolated compounds and the reaction conditions were typically as given in the example below.

Reaction of $Os_3(CO)_{10}(C_2H_2)$ *with hydride*

On treating a solution of $Os_3(CO)_{10}(C_2H_2)$ (0.110 g) in freshly distilled dry THF (30 cm^3) with a fourfold excess of $LiBHEt_3$ in THF (0.5 cm^3) at room temperature, the colour of the solution changed from bright orange to yellow. Trifluoroacetic acid (0.050 cm^3) was added after 8 h. After 20 h the solvent was removed under reduced pressure and chromatographic separation of the residue (SiO_2, t.l.c.) eluting with petroleum ether gave bands that yielded $Os_3H_2(CO)_9(C_2H_2)$ (0.005 g, 5%), $Os_3H(CO)_9(CHCHCH)$ (0.003 g, 3%), and $Os_3H(CO)_9(CH{=}C{=}CH_2)$ (0.002 g, 2%). Most of the material remaining on the baseline was eluted with a petroleum ether–chloroform–diethyl ether mixture (80:15:5 by volume) to give two bands. One remains unidentified while the other gave $Os_3H(CO)_9(CHCHCOH)$ (0.074 g, 68%) as pale yellow crystals. Addition of $LiBHEt_3$ at −78 °C followed by warming to room temperature did not materially alter the reaction products. The compounds $Os_3H(CO)_9(CH{=}C{=}CH_2)$ and $Os_3H(CO)_9(CHCHCH)$ appear identical to those formed by photolysis then thermolysis of $Os_3(CO)_{11}(CH_2CCH_2)$ which is formed itself from allene and $Os_3(CO)_{11}(MeCN)$ (Johnson *et al.* 1982).

We thank the S.E.R.C. for a research studentship and Johnson–Matthey Ltd for a generous gift of osmium tetraoxide.

REFERENCES

Aime, S., Deeming, A. J., Hurtshouse, M. B. & Backer-Dirks, J. D. J. 1982 *J. chem. Soc. Dalton Trans.*, pp. 1625–1629.

Arce, A. J. & Deeming, A. J. 1980 *J. chem. Soc. chem. Commun.*, pp. 1102–1103.

Azam, K. A., Choo Yin, C. & Deeming, A. J. 1978 *J. chem. Soc. Dalton Trans.*, pp. 1201–1206.

Choo Yin, C. & Deeming, A. J. 1975 *J. chem. Soc. Dalton Trans.*, pp. 2091–2096.

Churchill, M. R., DeBoer, B. G., Shapley, J. R. & Keister, J. B. 1976 *J. Am. chem. Soc.* **98**, 2357–2358.

Clauss, A. D., Shapley, J. R. & Wilson, S. R. 1981 *J. Am. chem. Soc.* **103**, 7387–7388.

Deeming, A. J. & Hasso, S. 1975*a* *J. organometall. Chem.* **88**, C21–C23.

Deeming, A. J. & Hasso, S. 1976*a* *J. organometall. Chem.* **114**, 313–324.

Deeming, A. J. & Hasso, S. 1976*b* *J. organometall. Chem.* **113**, C39–C42.

Deeming, A. J., Hasso, S. & Underhill, M. 1975*b* *J. chem. Soc. Dalton Trans.*, pp. 1614–1620.

Deeming, A. J. & Peters, R. 1982 *J. organometall. Chem.* (In the press.)

Deeming, A. J., Peters, R., Hurtshouse, M. B. & Backer-Dirks, J. D. J. 1982 *J. chem. Soc. Dalton Trans.*, pp. 1205–1211.

Dyke, A. F., Knox, S. A. R., Naish, P. J. & Taylor, G. E. 1980 *J. chem. Soc. chem. Commun.*, pp. 409–410.

Eisenstein, O. & Hoffmann, R. 1981 *J. Am. chem. Soc.* **103**, 4308–4320.

Finnimore, S. P., Knox, S. A. R. & Taylor, G. E. 1980 *J. chem. Soc. chem. Commun.*, pp. 411–412.

Gavens, P. D. & Mays, M. J. 1978 *J. organometall. Chem.* **162**, 389–401.

Granozzi, G., Tondello, E., Bertoncello, R., Aime, S. & Osella, D. 1982 (Submitted.)

Hanson, B. E., Johnson, B. F. G., Lewis, J. & Raithby, P. R. 1980 *J. chem. Soc. Dalton Trans.*, pp. 1852–1857.

Henrick, K., McPartlin, M., Deeming, A. J., Hasso, S. & Manning, P. 1982 *J. chem. Soc. Dalton Trans.*, pp. 899–906.

Johnson, B. F. G. (ed.) 1980 *Transition metal clusters*. London and New York: Wiley.

Johnson, B. F. G., Lewis, J., Raithby, P. R. & Sankey, S. W. 1982 *J. organometall. Chem.* **231**, C65–C69.

Kaesz, H. D., Knobler, C. B., Andrews, M. A., van Buskirk, G., Szostak, R., Strouse, C. E., Lin, Y. C. & Mayr, A. 1982 *Pure appl. Chem.* **54**, 131–144.

Kennedy, S., Alexander, J. J. & Shore, S. G. 1981 *J. organometall. Chem.* **219**, 385–395.

Shapley, J. R. & Keister, J. B., Churchill, M. R. & DeBoer, B. G. 1975 *J. Am. chem. Soc.* **97**, 4145–4146.

Steinmetz, G. R. & Geoffroy, G. L. 1981 *J. Am. chem. Soc.* **103**, 1278.