Carbon–Nitrogen Bond Cleavage in 1-Dimethylaminobut-2-yne and Derived Ligands in Triruthenium and Triosmium Clusters

Silvio Aime,* Giorgio Jannon, and Domenico Osella
Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio, 48, Torino 10125, Italy
Alejandro J. Arce and Antony J. Deeming *
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ

Dodecacarbonyltriruthenium reacts in refluxing cyclohexane with 1-dimethylaminobut-2-yne ($MeC\equiv CCH_2NMe_2$) to give good yields of the isomers $[Ru_3H(CO)_9(\mu_3\text{-}MeCCCHNMe_2)]$ (1) and $[Ru_3H(CO)_9(\mu_3\text{-}MeCCHCNMe_2)]$ (2) which are related in stoicheiometry (although perhaps not in structure) to known complexes containing μ_3-allenyl ($R^1C=C=CHR^2$) or diosmium-substituted μ_3-allyl (R^1CCHCR^2) ligands. The osmium analogue of complex (1) is obtained similarly from $[Os_3(CO)_{12}]$ but $[Os_3(CO)_{10}(MeCN)_2]$ reacts at room temperature with the alkyne giving $[Os_3H(CO)_9(\mu_3\text{-}MeC=C=CH_2)]$ by C–N bond cleavage. Rotation about the C–N bond in complex (1) in chloroform solution is restricted but the rate is accelerated by the addition of small amounts of CF_3CO_2H while, in neat CF_3CO_2H, compound (1) is protonated to give $[Ru_3H_2(CO)_9(MeCCCHNMe_2)]^+$ for which the rotation barrier is much higher. Neutralisation of acidic solutions of complex (1) gives up to 15% of the but-2-ynal compound $[Ru_3H_2(CO)_9(\mu_3\text{-}MeC_2CHO)]$ by hydrolysis. Compound (1) is converted totally into (2) in refluxing hexane but in the presence of H_2 hydrogenolysis of the C–N bond also occurs to give the compounds $[Ru_3H_2(CO)_9(\mu_3\text{-}MeC_2Me)]$, $[Ru_3H(CO)_9(\mu_3\text{-}MeC=C=CH_2)]$ and $[Ru_3H(CO)_9(\mu_3\text{-}MeCCHCH)]$.

The reaction of $[Ru_3(CO)_{12}]$ with $MeC\equiv CCH_2NMe_2$ to give compounds (1) and (2) has been briefly described[1] and similarly $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ react with $HC\equiv CCH_2NMe_2$ to give related compounds.[2] Initially we observed only hydrido-clusters from these reactions, with ligands containing carbon-bound NMe_2. However, in the terminal alkyne case the products were shown by spectroscopy and by *X*-ray structure determination for the ruthenium compound to be the complexes $[M_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}Me_2NCCCH_2)]$.[2] To form this type of compound there has been a hydrogen-atom shift from carbon to metal and a 1,3 shift of the NMe_2 group. This shift suggested the possibility of C–N bond-cleavage reactions to give nitrogen-free derivatives of these alkynes or possibly products in which the NMe_2 group has migrated to the metal. A number of reports have appeared on C–N cleavage reactions of alkylamines at, or induced by, transition-metal carbonyl clusters.[3-6] None appears to occur as readily as those we now describe in the direct room-temperature reaction of $MeC\equiv CCH_2NMe_2$ with $[Os_3(CO)_{10}(MeCN)_2]$ or by acid hydrolysis or hydrogenolysis of $[Ru_3H(CO)_9(MeCCCHNMe_2)]$, compound (1).

Results and Discussion

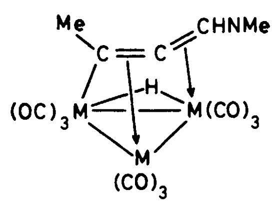
We have already reported that $[Ru_3(CO)_{12}]$ reacts readily with $MeC\equiv CCH_2NMe_2$ in refluxing cyclohexane (1 h) to give good yields of compounds (1) (50%) and (2) (40%).[1] Compound (1) is converted into (2) thermally in refluxing heptane. The related reaction of $[Os_3(CO)_{12}]$ with the same alkyne occurs in refluxing n-octane to give a yellow solution yielding after chromatography compound (3) (22%) which is directly analogous to compound (1) (Table).

Two other chromatographic bands gave two isomers with the formula $[Os_3(CO)_8L_2]$, where L is $MeC\equiv CCH_2NMe_2$, in 14 and 52% yield respectively. We are not yet sure of the true natures of these two isomers so, apart from minimal details of their preparation (Experimental section), we will leave further discussion to a later paper. No evidence for the formation of the osmium analogue of compound (2) in this reaction was found. Therefore excellent combined yields of products retaining N–C bonds were obtained both for ruthenium and osmium.

The complex $[Os_3(CO)_{10}(MeCN)_2]$ is much more reactive than $[Os_3(CO)_{12}]$ and reacts at room temperature with $MeC\equiv CCH_2NMe_2$ in chloroform. Remarkably the only product isolated by chromatography was the known allenyl compound $[Os_3H(CO)_9(MeC=C=CH_2)]$ (4) (20%).[7] No evidence for any of the products formed from the alkyne and $[Os_3(CO)_{12}]$ was obtained and neither was compound (4) observed in high-temperature reactions of $[Os_3(CO)_{12}]$. We cannot easily account for this C–N cleavage reaction since one would normally expect cleavage to be favoured at higher temperatures. Perhaps the more readily accessible co-ordination sites in $[Os_3(CO)_{10}(MeCN)_2]$ allow nitrogen co-ordination which is necessary for C–N cleavage to occur.

In the context of this cleavage reaction we describe reactions of compound (1) with CF_3CO_2H or with H_2 that also lead to products not containing nitrogen. Compounds (1)—(3) all have non-equivalent NMe groups and each give two ^1H n.m.r. singlets at low temperatures consistent with significant π donation from the NMe_2 group. The extent of donation is not clear but may be considerable as in $[Ru_3H(CO)_9(Me_2NCCCH_2)]$ which exists as the zwitterion (5) rather than the allenyl form (6) (*X*-ray structure[2]). Related zwitterionic representations could also be given for compounds (1)—(3) which might be more realistic than those given. However, the barrier to rotation about the C–N bond in compound (5) is very much greater than that for compound (1); an estimate of $\Delta G > 90$ kJ mol^{-1} for (5) is to be compared with a value of 57.7 kJ mol^{-1} for (1) which might indicate that the extent of π donation from NMe_2 in compound (1) is significantly less than that in (5). *X*-Ray determinations of the structures of compounds (1) and (2) are planned to assess this point more precisely.

We have observed that the barrier in compound (1) is reduced when acid is present. For example, the addition of small amounts of CF_3CO_2H (0.001—0.01 cm^3) to a solution of (1) in $CDCl_3$ (0.5 cm^3) gave no change in the spectrum other than a marked decrease in the temperature of coalescence, T_c,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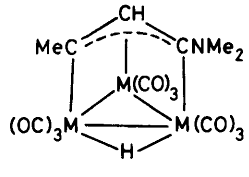
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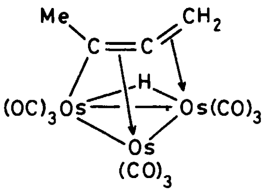
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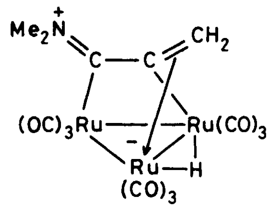
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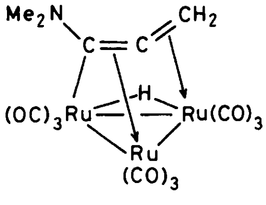
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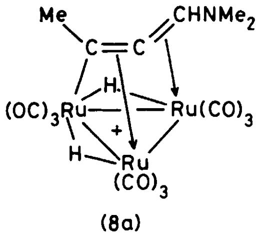
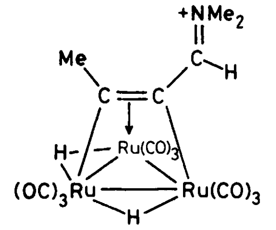
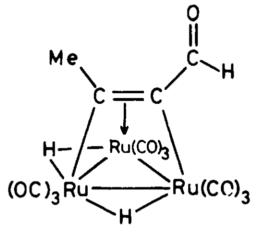

(8a)


(8b)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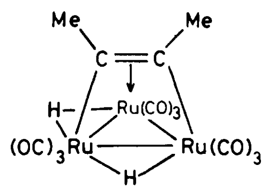
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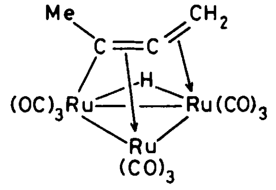
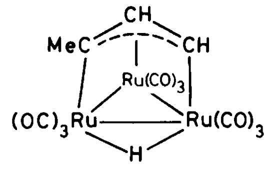

(11)


(12)

of the NMe_2 singlets. The larger amounts of acid led to a decrease of 40 to 50 °C in T_c. We believe that the explanation of this acid-catalysed rotation about the C–N bond is a rapid and reversible protonation at nitrogen in compound (1) to give a transient species $[Ru_3H(CO)_9(MeC{=}C{=}CHNHMe_2)]^+$ (7) in which very ready rotation about the C–N bond occurs. Since there is no change in the spectrum other than in the value of T_c, no significant amounts of the transient species (7) are generated. Other slower reactions complicate the picture. When using CF_3CO_2D the MeCCC*H*NMe_2 ^1H n.m.r. signal at δ 7.31 decreases in intensity because of incorporation of deuterium at this site. Presumably there is an equilibrium quite separate from that involving (7) and possibly entailing hydrogen-atom transfer between the metal and the carbon atom α to the nitrogen atom. Certainly protonation at the metal atoms is not the cause of the acid-catalysed methyl exchange. This would have had the reverse effect of increasing π donation from NMe_2 and increasing the rotation barrier.

On increasing the acidity of the solution by using neat CF_3CO_2H, compound (1) dissolves to give a yellow-brown solution in which compound (7) is not observed but rather another isomer, the protonated species (8), is present. Our interpretation is that strong acid is needed for most of compound (1) to be protonated and that although (7) is formed more rapidly it is less stable than the protonated species (8). Compound (8), $[Ru_3H_2(CO)_9(MeCCCHNMe_2)]^+$, has been characterised by its ^1H and ^{13}C n.m.r. spectra and ν(CO) i.r. absorptions [*ca.* 40 cm^{-1} higher than in (1)], see Table and Experimental section. Two sharp NMe_2 ^1H n.m.r. singlets are observed at room temperature for solutions of compound (8) in CF_3CO_2H–SO_2 mixtures and up to 70 °C. The rotational barrier about the C–N bond has been considerably increased by protonation at the metal atoms as expected so that (8b) may be a rather more reasonable description of the structure than (8a). No hydride n.m.r. signal is observed at room temperature because this is close to the coalescence temperature. Two hydride signals [δ −15.50 and −19.15; not very different from those for compound (10), see later] are observed below −15 °C and a single resonance resulting from coalescence is observed above +50 °C. Hydride exchange is occurring faster than NMe_2 exchange either by hydride migration or by rotation of the whole $MeCCCHNMe_2$ ligand with respect to the Ru_3 triangle. Removal of the solvent gives a yellow-brown oil which remains as the protonated species (8) when redissolved in $CDCl_3$–CD_2Cl_2 mixtures. The ^{13}C n.m.r. spectrum of an isotopically enriched sample of (8) at

Table. Infrared and ^{1}H n.m.r. data

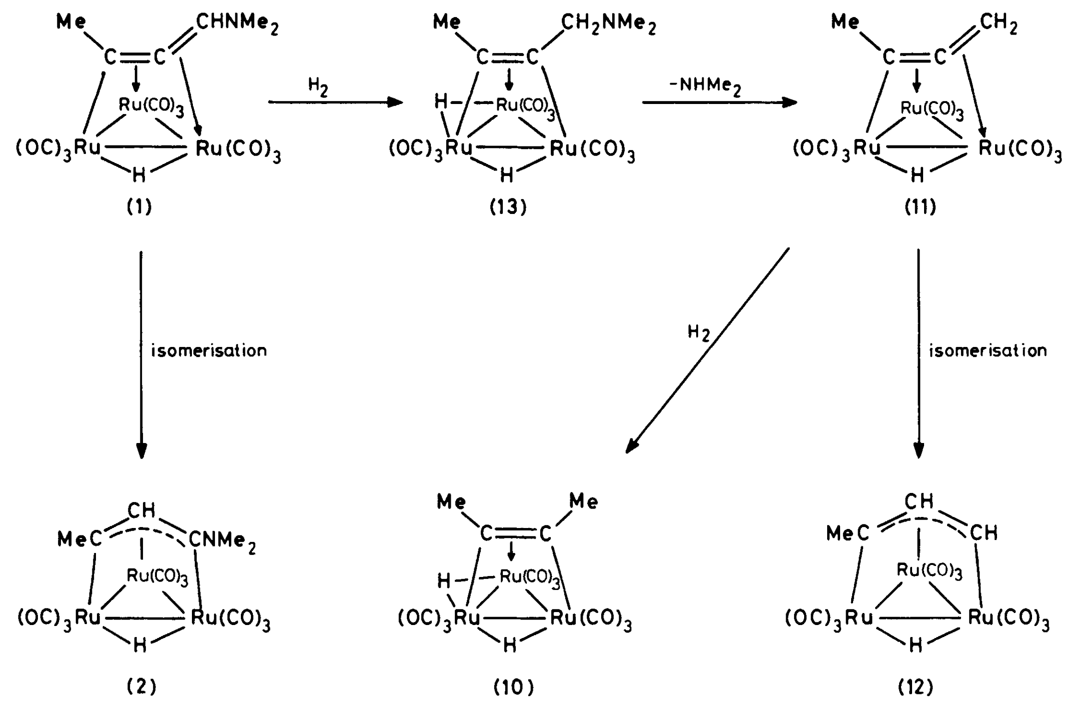
	ν(CO) [a]/cm^{-1}	^{1}H N.m.r. data [b]	
		δ/p.p.m.	Assignment
(1) $[Ru_3H(CO)_9(MeCCCHNMe_2)]$	2 083m, 2 053s, 2 030vs, 2 013m, 2 000m, 1 988w	7.31(s)	CH
		3.30(s)	NMe
		2.95(s)	NMe
		2.52(s)	CMe
		$-$18.83(s)	RuH
(2) $[Ru_3H(CO)_9(MeCCHCNMe_2)]$	2 089m, 2 060s, 2 034vs, 2 018m, 2 004m, 1 996m, 1 974w	6.00(d)	CH [c]
		3.55(s)	NMe
		3.30(s)	NMe
		2.72(s)	CMe
		$-$17.58(d)	RuH [c]
(3) $[Os_3H(CO)_9(MeCCCHNMe_2)]$	2 082m, 2 052s, 2 028s, 2 004s, 1 988m, 1 973ms, 1 952w	7.13(s)	CH
		3.36(s)	NMe
		3.04(s)	NMe
		2.67(s)	CMe
		$-$18.80(s)	OsH
(8) $[Ru_3H_2(CO)_9(MeCCCHNMe_2)]^+$	2 094s, 2 074vs, 2 030vs, 2 006m [d]	8.34(s)	CH
		3.92(s)	NMe
		3.89(s)	NMe
		2.89(s)	CMe
		$-$15.50(br)	RuH
		$-$19.15(br)	RuH
(9) $[Ru_3H_2(CO)_9(MeC{=}CCHO)]$ [e]	2 110m, 2 081s, 2 061vs, 2 042s, 2 016s, 1 996m, 1 673wm	10.01(s)	CHO
		3.21(s)	CMe
		$-$16.14(d)	RuH
		$-$19.82(d)	RuH
(10) $[Ru_3H_2(CO)_9(MeC{=}CMe)]$ [f]	2 103m, 2 075s, 2 052vs, 2 039s, 2 026m, 2 012s, 2 005m, 1 989m	2.52(s)	CMe
		$-$15.12(d)	RuH [g]
		$-$19.50(d)	RuH
(11) $[Ru_3H(CO)_9(MeC{=}C{=}CH_2)]$ [h]	2 095m, 2 066s, 2 043s, 2 026s, 2 010m, 1 999m, 1 986w		

[a] Recorded in cyclohexane solution except for compound (8). [b] Recorded in $CDCl_3$ except for compound (8) for which the data are for CF_3CO_2H–SO_2 solutions at -40 °C. [c] J = 4.0 Hz. [d] Recorded in a $CHCl_3$–CF_3CO_2H mixture with the same mixture in the i.r. reference cell. Since peaks are rather broad, weak absorptions could not be detected. [e] N.m.r. recorded at -30 °C. Coalescence around 25 °C leads to a averaged hydride singlet at 60 °C. [f] N.m.r. recorded at -30 °C. At 21 °C a coalesced hydride singlet at δ -17.40 is observed. [g] J = 3.0 Hz. [h] Not obtained without contamination by the known isomer (12).

-50 °C gave seven CO signals in ratio 1 : 1 : 3 : 1 : 1 : 1 : 1 (see Experimental section) consistent with a static structure allowing for some accidental overlap. A shift to higher frequencies and a reduced range of ^{13}C chemical shifts is noted on protonation. At room temperature coalescence to give a 1 : 2 : 6 pattern seems consistent with an oscillatory motion equilibrating two $Ru(CO)_3$ units with localised CO exchange at each of these.

Solutions of compound (8) in CF_3CO_2H or in $CHCl_3$–CF_3CO_2H mixtures were neutralised by pouring them into ethanol over solid sodium hydrogencarbonate followed by chromatography of the residue on silica after removal of the original solvent. There was only a low recovery of the starting compound (1) but, as well as other unidentified products, we obtained variable yields of a new cluster (9). The Experimental section describes a typical reaction leading to about 15% of this compound; use of neat CF_3CO_2H as the initial solvent gave very low yields. Compound (9) has been characterised spectroscopically as the μ_3-but-2-ynal compound $[Ru_3H_2(CO)_9(MeCCCHO)]$ containing a non-co-ordinated formyl group [ν(CO) 1 673 cm^{-1}; ^{1}H n.m.r. singlet at δ 10.01]. Compound (9) is like the well known type of alkyne cluster found in triosmium chemistry but rare in triruthenium chemistry. It shows expected characteristics such as exchange of the non-equivalent hydride ligands and is closely related to $[Ru_3H_2(CO)_9(\mu_3\text{-}C_8H_{12})]$ (*X*-ray structure), a cyclo-octyne complex formed from cyclo-octene.[8] Compound (9) is a product of the acid-induced hydrolysis of compounds (1) or (8) and was also obtained directly from (1) in refluxing hexane in the presence of aqueous CF_3CO_2H. If the hydrolysis route passes through the hydroxyallenyl compound $[Ru_3H(CO)_9(\mu_3\text{-}MeC{=}C{=}CHOH)]$, a rapid hydrogen-atom transfer must give compound (9), whereas hydroxy-compounds such as $[Os_3H(CO)_9(\mu_3\text{-}CHCHCOH)]$ [like compound (2) but with NMe_2 replaced by OH] are quite stable.[9,10]

As well as being hydrolysed, the C–N bond of compound (1) undergoes hydrogenolysis, providing a route to otherwise unobtainable triruthenium clusters. In refluxing hexane compound (1) slowly isomerises to compound (2). If H_2 is bubbled through a refluxing hexane solution of (1), there is a 50% isomerisation to compound (2), and also about a 40% total conversion into three compounds, (10)—(12), not containing nitrogen. Compound (10) is the new but-2-yne cluster $[Ru_3H_2(CO)_9(\mu_3\text{-}MeC_2Me)]$, characterised by the spectra given in the Table. While the triosmium analogue is known,[7] triruthenium compounds of this type are not easily accessible and this particular compound is new. Compound (12) was easily characterised by its ν(CO) absorptions and ^{1}H n.m.r. spectra as the known complex $[Ru_3H(CO)_9(MeCCHCH)]$, compounds of this type being normally formed by 1,2-hydrogen-atom shift reactions of the allenyl isomers. The allenyl precursor in this case would be $[Ru_3H(CO)_9(MeC{=}C{=}CH_2)]$. We have shown that compound (11) is readily converted into (12) in refluxing hexane and because of this it was not possible to obtain pure samples of compound (11) totally free from contamination by (12). On



Scheme.

this chemical evidence and by comparison of spectroscopic data with those of the osmium analogue, compound (4), and related triruthenium compounds, we have been able to identify compound (11) as [$Ru_3H(CO)_9(MeC{=}C{=}CH_2)$]. The Scheme illustrates the probable route to compounds (10)—(12). Hydrogenation of compound (1) competes with its isomerisation to (2) which we have shown to be inert to hydrogenation under the reaction conditions and so is not an intermediate in the formation of compounds (10)—(12). Compound (11) is likely to be the primary hydrogenolysis product since (10) and (12) would be formed from it under the reaction conditions. The involvement of compound (13) as shown in the Scheme is speculative (it was not detected) but it is the most obvious immediate hydrogenation product of compound (1) and it would seem that hydrogen-atom addition to the carbon atom α to nitrogen must precede C–N bond cleavage.

Experimental

Compounds (1) and (2) were obtained as described previously.[1]

Reaction of [$Os_3(CO)_{12}$] *with 1-Dimethylaminobut-2-yne.*—A solution of [$Os_3(CO)_{12}$] (0.210 g) and $MeC{\equiv}CCH_2NMe_2$ (0.09 g) in octane was heated under reflux for 3 h. Removal of the solvent gave a yellow-orange residue which was separated by t.l.c. (SiO_2; eluant, pentane–diethyl ether, 1 : 1 v/v) to give three bands. The slowest moving of these gave [$Os_3H(CO)_9(MeCCCHNMe_2)$] (3) as yellow crystals (0.045 g, 22%). The other two bands gave two triosmium clusters each containing two dimethylaminobutyne ligands: [$Os_3(CO)_8(C_{12}H_{22}N_2)$], first isomer, orange crystals (0.030 g, 14%) (Found: C, 24.3; H, 2.2; N, 2.5. $C_{20}H_{22}N_2O_8Os_3$ requires C, 24.3; H, 2.25; N, 2.8%), ν(CO) (C_6H_{12}) at 2 073m, 2 040s, 1 998m, 1 981m, 1 976vs, 1 967w, 1 937w, and 1 916m cm^{-1}; second isomer, orange crystals (0.110 g, 52%) (Found: C, 24.6; H, 2.2; N, 2.5%), ν(CO) (C_6H_{12}) at 2 073m, 2 038s, 1 995m, 1 981 (sh), 1 978s, 1 968w, 1 940w, and 1 919m cm^{-1}.

Reaction of [$Os_3(CO)_{10}(MeCN)_2$] *with 1-Dimethylaminobut-2-yne.*—A solution of the bis(acetonitrile) complex with an equimolar amount of the aminoalkyne in chloroform was allowed to stand at room temperature. Removal of the solvent after 24 h and chromatography of the residue on silica (eluant: pentane–diethyl ether, 4 : 1 v/v) gave [$Os_3H(CO)_9(\mu_3\text{-}MeC{=}C{=}CH_2)$] as yellow crystals (20%), identified by comparison of its i.r. and ^1H n.m.r. spectra with those of authentic samples.

Treatment of [$Ru_3H(CO)_9(\mu_3\text{-}MeC{=}C{=}CHNMe_2)$] (1), *with Trifluoroacetic Acid.*—Proton n.m.r. spectra (Table) of yellow-brown solutions of compound (1) in CF_3CO_2H show that it has dissolved to give [$Ru_3H_2(CO)_9(MeCCCHNMe_2)$]$^+$, compound (8). Removal of the solvent by a flow of nitrogen gave a brown oil which dissolved to give compound (8) in solution. The ^{13}C n.m.r. spectrum of a ^{13}C-enriched sample in $CDCl_3$–CD_2Cl_2 at −50 °C gave signals at δ 192.5(1), 191.3(1), 190.4(3), 189.9(1), 188.7(1), 185.8(1), and 184.9(1) p.p.m. (CO signals with intensities in parentheses). Compound (1) (*ca.* 0.04 g) was dissolved in chloroform (2 cm^3) and trifluoroacetic acid (0.2 cm^3) added. After a short time at room temperature the solution was diluted to 10 cm^3 with ethanol–chloroform (1 : 3 v/v) and an excess of solid $NaHCO_3$ added. The filtered solution was reduced to a small volume and separated by t.l.c. (SiO_2) to give [$Ru_3H_2(CO)_9(MeC_2CHO)$], compound (9), as a yellow solid (10—15%). The parent molecular ion was observed in the mass spectrum and other spectral details are given in the Table.

Reaction of Compound (1) *with Hydrogen.*—Hydrogen gas was bubbled through a refluxing solution of compound (1) in n-hexane for 6 h. Chromatographic work-up gave [$Ru_3H(CO)_9(MeCCHCNMe_2)$], compound (2), as an orange solid (50%) with spectra the same as those of the compound formed in the absence of hydrogen (Table). Three other compounds were obtained (accounting for 30—

40% of starting material): $[Ru_3H_2(CO)_9(MeC_2Me)]$, (10); $[Ru_3H(CO)_9(MeC{=}C{=}CH_2)]$, (11); and $[Ru_3H(CO)_9(MeCCHCH)]$, (12), eluted in that order on silica. Each gave the parent molecular ion in its mass spectrum and was characterised by spectra given in the Table. Compound (11) was always contaminated with compound (12) so the reported spectra are less reliable since absorptions due to (12) have had to be subtracted.

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