Reaction Chemistry of Alkynes with the Tris(acetonitrile)-ruthenium Cluster $[Ru_3(CO)_9(MeCN)_3]$

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The reactions of acetylene, monosubstituted alkynes HC_2R (R = Ph and $SiMe_3$) and disubstituted alkynes C_2RR' (R = R' = Me or Ph, R = Me, R' = Et) with the tris(acetonitrile)-substituted cluster $[Ru_3(CO)_9(MeCN)_3]$ have been studied. Monosubstituted alkynes form acetylide complexes $[Ru_3H(CO)_9(C_2R)]$ in high yield. Disubstituted alkynes undergo [2 + 2 + 2] cyclotrimerisation reactions to yield $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6R_3R'_3)]$ complexes in good yield. These complexes contain an aromatic, face-capping, group co-ordinated to the triruthenium cluster.

One of the keys to controlled synthetic ruthenium carbonyl cluster chemistry is the preparation of stable intermediates that allow displacement of ligand groups under mild conditions, thus avoiding the extreme temperatures or pressures usually required for direct substitution of carbonyl groups.[1] We have recently reported the preparation of the tris(acetonitrile)-substituted triruthenium compound $[Ru_3(CO)_9(MeCN)_3]$ **1**.[2] The synthetic potential of this reagent in the reaction with acetylenes is illustrated here. We present the synthesis of a number of acetylide compounds from reactions of **1** with monosubstituted alkynes, and complexes of the form $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6R_3R'_3)]$ (R = R' = Me or Ph; R = Me, R' = Et) from **1** and disubstituted alkynes.

This work comes at a time when there is interest in multisite cluster-bound alkyne compounds as models for chemisorption of alkynes on transition-metal surfaces and for the activation and reduction of the carbon–carbon triple bond.[3] The clusters also display the ability to act as templates for the [2 + 2 + 2] cyclotrimerisation of alkynes to form co-ordinated benzenes and to model the adsorption, at surface atoms, of such organic species in extended metal arrays.[4]

Results and Discussion

In the reaction between $[Ru_3(CO)_9(MeCN)_3]$ **1** and alkynes two different types of product can be obtained depending on the presence or absence of a terminal hydrogen on the alkyne. We will first discuss the chemistry of monosubstituted alkynes.

Reaction of acetylene with complex **1** at low temperature leads to the formation of a deep orange solution from which known two compounds $[Ru_3H(CO)_9(C_2H)]$ **2** and $[Ru_3(CO)_9(\mu\text{-}CO)(C_2H_2)]$ **3**, were isolated and characterised from their previously reported spectroscopic data.[5] In this reaction complex **3** is most probably formed by the scavenging of CO from the solution. Reaction of acetylene with **1** under reflux leads to the near-quantitative generation of **2**, a small proportion, approximately 5%, of the face-capping benzene complex $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$ **4** also being formed.[6]

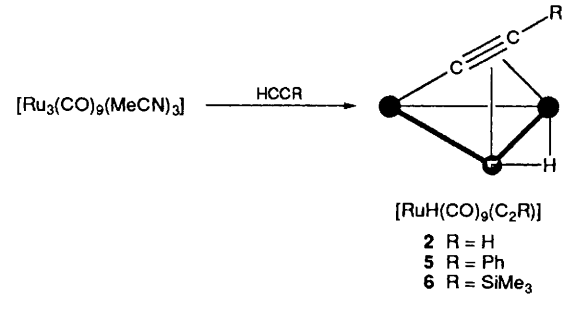
The ^{13}C NMR spectrum of the acetylide complex **2** was observed and comparisons between free and co-ordinated acetylene made (see Table 1). Considering the structure of **2**, five carbonyl environments would be expected in the ^{13}C NMR spectrum, however only three are observed at room temperature, at δ 197.8, 188.5 and 182.7. This may be rationalised in terms of a fluxional process involving the carbonyl groups at each metal centre at room temperature as has been observed previously for the complex $[Ru_3H(CO)_9(C_2Bu^t)]$.[8] For the acetylenic signals, large shifts are seen for the co-ordinated centres with signals observed at δ 36.5 (C≡*C*H) and 127.2 (*C*≡CH) for **2** as compared to δ 71.9 for free acetylene. Sources of the shift in the resonance on co-ordination include changes in charge density on the ligand atoms, changes in the intraligand π-bond orders, and changes in the hybridisation states of metal-bonded carbon atoms, or anisotropic effects.[9]

The formation of the acetylide complex **2**, in the reaction of **1** with acetylene was not unexpected due to the relative acidity of the acetylenic protons; the reaction of acetylene with $[Ru_3(CO)_{12}]$ yielded **2**.[7] The acidity of the terminal proton dominates the chemistry of terminal acetylenes and, therefore, appears to inhibit the formation of the face-capping benzene compound **4**.

It is interesting to compare the results documented here with those from the reaction of the bis(acetonitrile) complex $[Ru_3(CO)_{10}(MeCN)_2]$ with acetylene. In this case, at room temperature or below, $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C_2H_2)]$ **3** is formed in high yield which, upon heating, is readily converted into the acetylide compound **2**.[1]

As may be anticipated from above, the reaction of complex **1** with phenyl- and trimethylsilyl-acetylene leads to the formation of the acetylide complexes $[Ru_3H(CO)_9(C_2Ph)]$ **5**[7] and $[Ru_3H(CO)_9(C_2SiMe_3)]$ **6**, respectively. In this case there is no evidence for the formation of $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-alkyne})]$ complexes or face-capping substituted benzene clusters. This may be associated with the increased acidity of the acetylinic proton in phenyl- and trimethylsilyl-acetylene.

The formation of the acetylide clusters is illustrated in Scheme 1 and spectroscopic data for the compounds **2**, **5** and **6** are shown in Table 1.



$[RuH(CO)_9(C_2R)]$
2 R = H
5 R = Ph
6 R = $SiMe_3$

Scheme 1 Preparation of acetylide clusters by reaction of monosubstituted acetylenes with $[Ru_3(CO)_9(MeCN)_3]$

Table 1 Spectroscopic data for compounds **2–9**

	Compound	Infrared,[a] $\tilde{\nu}_{CO}$/cm^{-1}	NMR,[b] δ	Mass, *m/z*[c]
2	$[Ru_3H(CO)_9(C_2H)]$[5]	2094m, 2064vs, 2054vs, 2022vs, 2012vs, 1987m	^{1}H: 10.48 (s), −19.72 (s) ^{13}C: 36.5 (CH), 127.2 (*C*≡CH), 197.8, 188.5, 182.7 (CO)	581 (581)
3	$[Ru_3(CO)_9(\mu\text{-}CO)(C_2H_2)]$[5]	2064vs, 2052vs, 2038s, 2011m, 1989w, 1895m	^{1}H: 8.61 (s)	
4	$[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$[6]	2070m, 2026vs, 1996s, 1976vs	^{1}H: 4.53 (s)	658 (657)
5	$[Ru_3H(CO)_9(C_2Ph)]$[7]	2098m, 2070vs, 2055vs, 2020vs, 2004m, 1992m	^{1}H: 7.18 (m), −21.4 (s)	652 (653)
6	$[Ru_3H(CO)_9(C_2SiMe_3)]$	2099m, 2074vs, 2050vs, 2020vs, 2009s, 1982m	^{1}H: 0.34 (s), −22.5 (s)	718 (717)
7	$[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6Me_6)]$	2070m, 2038vs, 2027m, 1995s, 1970s	^{1}H: 2.24 (s) ^{13}C: 30.9 (ring C), 29.6 (Me), 20.7 (CO)	
8	$[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6Ph_6)]$	2060m, 2043vs, 2017m, 1988s, 1977vs	^{1}H: 7.1 (m), 7.05 (m), 6.94 (m)	
9	$[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6Me_3Et_3)]$	2060m, 2037vs, 2025m, 1998s, 1987s	^{1}H: 2.43 (q) 2.25 (s), 1.83 (t)	

[a] In CH_2Cl_2. [b] In $CDCl_3$. [c] Calculated values in parentheses.

The reaction chemistry of disubstituted alkynes with complex **1** was investigated using diphenylacetylene and but-2-yne (dimethylacetylene) and pent-2-yne (ethylmethylacetylene). Reaction with but-2-yne leads, within 2 h, to a deep orange solution with a similar IR spectrum to that of the face-capped benzene cluster **4**, and it is suggested that the hexamethylbenzene cluster $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6Me_6)]$ **7** is formed. The ^{1}H NMR and mass spectra are also consistent with this formulation. Additional evidence for a face-capping mode of co-ordination is obtained from ^{13}C NMR spectroscopy which shows three singlets, at δ 207.0 (corresponding to the carbonyl groups), 30.9 (corresponding to the methyl resonances) and 29.6 (corresponding to the carbons of the aromatic ring). This result compares favourably with the cases of $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$ and $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_5Me)]$ which show resonances for the carbons of the aromatic ring between δ 30 and 35. It is interesting also to compare the ^{13}C NMR data for **7** with those for free dimethylacetylene and $[Ru_3(CO)_{10}(C_2Me_2)]$, the former showing two singlets at δ 16.5 ($H_3CC{\equiv}CCH_3$) and 131.5 ($H_3CC{\equiv}CCH_3$), the latter showing considerable shift on co-ordination with signals at δ 1.7 ($H_3CC{\equiv}CCH_3$) and 73 $H_3CC{\equiv}CCH_3$).[10] Owing to the instability of **7**, it has not been possible to characterise the product fully by use of mass spectroscopy and elemental analysis, nor has it been possible to obtain low-temperatue ^{13}C NMR spectra due to solubility problems.

Complex **7** is relatively unstable and, upon standing in solution over 2 d or refluxing for an extended period, decomposition occurs yielding free hexamethylbenzene in solution, the latter being characterised by mass spectroscopy.

Reaction of complex **1** with diphenylacetylene leads to the corresponding hexaphenylbenzene cluster $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6Ph_6)]$ **8**. This formulation is consistent with the NMR and mass spectroscopic data. The ^{1}H NMR spectrum shows three multiplets centred around δ 7.05 constituting a high-field shift relative to the signals of free hexaphenylbenzene (centred around δ 7.2) on coordination. This is less marked than in the case of co-ordination of benzene to a triruthenium system.[5] This difference may be explained by the increased distance between the hydrogen centres and the co-ordinated aromatic ring, therefore decreasing the effects of co-ordination on the attached protons and decreasing the field change (Δδ). This is further illustrated in the case of co-ordination of toluene to triosmium systems where Δδ for the methyl group (0.3 ppm) is significantly smaller than that for the ring protons (2.7 ppm).[4]

As expected, complex **8** is considerably less stable that the hexamethyl analogue **7** on steric grounds and, on extended reflux, free hexaphenylbenzene may be liberated with concomitant decomposition of the cluster. Again, because of the instability of **8**, full characterisation by mass spectroscopy and elemental analysis was not possible.

Reaction of complex **1** with ethylmethylacetylene leads to the formation of the corresponding 1,3,5-triethyl-2,4,6-trimethylbenzene complex $[Ru_3(CO)_9(C_6Me_3Et_3)]$ **9**, as characterised by IR and ^{1}H NMR spectroscopy, and it is of interest that only one isomer of the substituted benzene appears to be formed. As in the case of the hexamethyl and hexaphenyl analogues, **9** is unstable on extended reflux liberating the substituted arene.

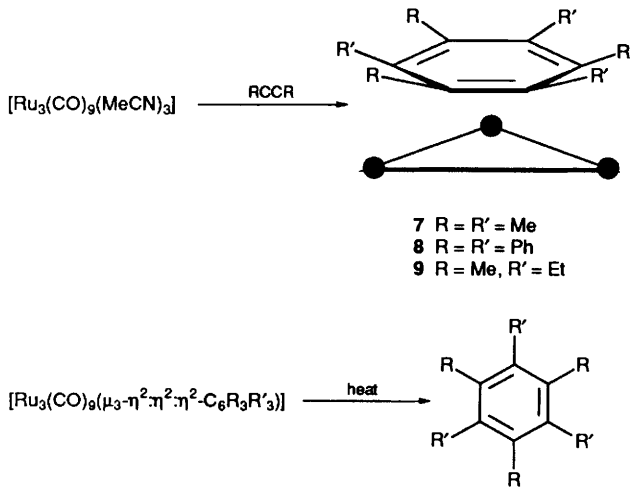
The formation of the substituted benzene clusters is illustrated in Scheme 2 and spectroscopic data for compounds **7–9** are listed in Table 1.

In conclusion, reaction of monosubstituted acetylenes (RC≡CH) with the tris(acetonitrile) complex **1** leads predominantly to the formation of the corresponding acetylide $[Ru_3H(CO)_9(C{\equiv}CR)]$ as is the case for the mono- and bis-acetonitrile analogues. With disubstituted acetylenes (RC≡CR) the corresponding hexasubstituted benzene clusters $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6R_6)]$ are formed. Heating these clusters leads to the liberation of the free substituted benzene. The fact that the substituted benzene can be easily liberated from the cluster is of particular interest since [2 + 2 + 2] cyclotrimerisation of alkynes attracts considerable attention both in organic synthesis and in the use of metal catalysts for such reactions.

Experimental

Unless otherwise stated, all reactions were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques and solvents were distilled prior to use. The complex $[Ru_3(CO)_9(MeCN)_3]$ **1** was prepared by published methods.[2] Alkynes were used as obtained. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform spectrometer using 0.5 mm solution cells, ^{1}H NMR spectra using a Bruker AM400 Fourier-transform spectrometer and mass spectra on an AEI MS 12 or a FAB MS 902 instrument. Routine separations of products were performed by thin-layer chromatography on laboratory-prepared glass plates coated to a thickness of 1.0 mm with Merck Kieselgel 60 F_{254}. All spectroscopic data are listed in Table 1.

Reactions of $[Ru_3(CO)_9(MeCN)_3]$ **1**.—*With acetylene at room temperature.* Acetylene was bubbled through a solution of the tris(acetonitrile) cluster **1** (50 mg) in dichloromethane for



Scheme 2 Preparation of substituted benzene clusters by reaction of disubstituted acetylenes with $[Ru_3(CO)_9(MeCN)_3]$

about 30 min. The solvent was removed *in vacuo* and the residue purified by TLC using dichloromethane–hexane (60:40). The main product was spectroscopically characterised as $[Ru_3H(CO)_9(C_2H)]$ **2** and was isolated as a deep orange powder (70%) (Found: C, 22.45; H, 0.30; O, 24.95. Calc. for $C_{11}H_2O_9Ru_3$: C, 22.70; H, 0.35; O, 24.80%), with a small amount (5%) of $[Ru_3(CO)_9(\mu\text{-}CO)(C_2H_2)]$ **3** as a second product.

With HCCR (R = Ph *or* $SiMe_3$) *at room temperature.* A solution of complex **1** (50 mg) in dichloromethane was treated with an excess of HCCR (20 mg) and the solution stirred until no further darkening in the colour was observed (*ca.* 20 min). The solvent was removed *in vacuo*. Purification of the residue by thin-layer chromatography using dichloromethane–hexane (70:30) yielded one product in 95% yield. The product was spectroscopically characterised as $[Ru_3H(CO)_9(C_2R)]$ (R = Ph **5** or $SiMe_3$ **6**).

With acetylene at elevated temperature. Acetylene was bubbled through a refluxing solution of cluster **1** (50 mg) in dichloromethane for about 1 h. The solvent was removed *in vacuo* and the residue purified by TLC using dichlomethane–hexane (60:40). Complex **2** was obtained as the main product (70%), with a small amount (*ca.* 2%) of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **4** isolated as a second product.

With HCCR (R = Ph *or* $SiMe_3$) *at elevated temperature.* A refluxing solution of cluster **1** (50 mg) in dichloromethane was treated with an excess of HCCR (20 mg) and heating maintained for 3 h. The solvent was removed *in vacuo*. Purification of the residue by thin-layer chromatography using dichloromethane–hexane (60:40) yielded 95% of one product spectroscopically characterised as $[Ru_3H(CO)_9(C_2R)]$ (R = Ph **5** or $SiMe_3$ **6**).

With RCCR′ (R = R′ = Me *or* Ph; R = Me, R′ = Et). A refluxing solution of cluster **1** (50 mg) in dichloromethane was treated with 3 equivalents of RCCR (42 mg) and heating maintained for 3 h yielding 75% of one major product $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6R_3R'_3)]$ (R = R′ = Me **7** or Ph **8**; R = Me, R′ = Et **9**) as well as some decomposition products.

Extended Heating of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6R_3R'_3)]$ (R = R′ = Me *or* Ph; R = Me, R′ = Et).—A dichloromethane solution of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6R_3R'_3)]$ (30 mg) was refluxed for 6 h. Analysis of the brown product mixture by mass spectroscopy showed the presence of free arene.

Acknowledgements

We thank Dr. J. Köhler for his advice during the period of this work. We acknowledge the financial support of the EPSRC (N. E. L.) and are grateful to Johnson Matthey plc for a loan of ruthenium trichloride.

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Received 5*th April* 1995; *Paper* 5/02196K