# Variable Co-ordination Behaviour of Ethyne and Other Alkynes Towards the Diruthenium Complexes $[Ru_2(\mu\text{-}CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ and $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{(RO)_2PN(Et)P(OR)_2\}_2]$ (sb = semi-bridging, R = Me or $Pr^i$)†

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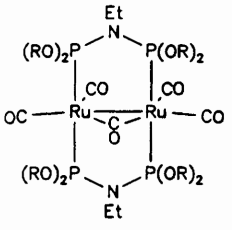
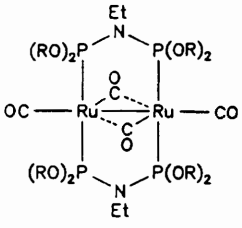
The reaction of ethyne with $[Ru_2(\mu\text{-}CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ in toluene at 80 °C or with $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or $Pr^i$, sb = semi-bridging), in toluene at room temperature, affords almost exclusively the ethenediyl-bridged species $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ for R = Me and the vinylidene-bridged product $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CH_2)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ for R = $Pr^i$; a second, minor product is also formed in each of these reactions and was identified as $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CH_2)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}_2]$ and $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ respectively. The reactions of $[Ru_2(\mu\text{-}CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ and $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{(RO)_2PN(Et)P(OR)_2\}_2]$ with the terminal alkynes $MeC{\equiv}CH$, $PhC{\equiv}CH$ and $MeO_2CC{\equiv}CH$ also afford mixtures of alkenediyl- and vinylidene-bridged products with the relative yields of these isomers being dependent on the identity of the alkyne and of the bridging diphosphazane ligand. On the other hand reaction with the internal alkyne $MeO_2CC{\equiv}CCO_2Me$ gives solely the alkenediyl-bridged product $[Ru_2(\mu\text{-}\sigma^2\text{-}MeO_2CC{=}CCO_2Me)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ irrespective of the diphosphazane ligand involved. Possible mechanisms for the formation of the two types of products are described. The crystal structure of $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}_2]$ is reported.

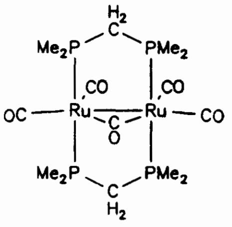
We have established previously that the diruthenium diphosphazane-bridged compounds $[Ru_2(\mu\text{-}CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me, Et, $Pr^i$, *etc.*) **1**,[1] substituted derivatives of diruthenium nonacarbonyl, are sufficiently electron rich to react readily at room temperature with a wide range of electrophiles including protons,[2] metal salts,[3] halogens[4] and nitrosyl ions[5] as well as with electron-acceptor ligands such as quinones[6] and tetracyanoethylene and tetracyanoquinodimethane.[7] More forceful conditions are required for the reaction of these pentacarbonyl species with nucleophilic agents however and even the reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}_2]$ with 2,6-dimethylphenyl isocyanide to afford $[Ru_2(\mu\text{-}CO)(CO)_3(CNC_6H_3Me_2\text{-}2,6)\{(MeO)_2PN(Et)P(OMe)_2\}_2]$ requires a reaction temperature of at least 50 °C and a reaction time of at least 6 h. We have also established that under appropriate reaction conditions these diruthenium pentacarbonyl derivatives can be decarbonylated to the co-ordinatively unsaturated species $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{(RO)_2PN(Et)P(OR)_2\}_2]$ (sb = semi-bridging) **2** and that the latter are very susceptible to both nucleophilic as well as electrophilic attack under mild conditions.[8]



| | R |
|---|---|
| 1a | Me |
| 1b | Et |
| 1c | $Pr^i$ |



| | R |
|---|---|
| 2a | Me |
| 2b | $Pr^i$ |



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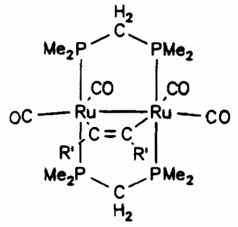

| | R' |
|---|---|
| 4a | Ph |
| 4b | $CO_2Me$ |

Johnson and Gladfelter[9] have recently reported the synthesis of the dmpm-bridged (dmpm = $Me_2PCH_2PMe_2$) diruthenium compound $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dmpm)_2]$ **3** and showed that this highly electron-rich species reacts readily with the relatively non-activated alkyne, diphenylacetylene, as well as with the activated electron-poor alkynes, methyl propiolate, dimethyl- and diethyl-acetylenedicarboxylate and hexafluorobut-2-yne, to afford, as the thermodynamically stable products, diruthenacyclobutene derivatives **4**, resulting from the formal *cis*-dimetallation of the alkynes.[9,10] A different co-ordination behaviour is observed on reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ and $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{(RO)_2PN(Et)P(OR)_2\}_2]$ with mono-substituted alkynes however. The results of this investigation are reported here; some of these results have been reported as a preliminary communication.[11]

## Results and Discussion

*Synthetic Studies.*—(*i*) *Reaction of* $[Ru_2(\mu\text{-}CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ *with ethyne.* Treatment of $[Ru_2(\mu\text{-}CO)$-

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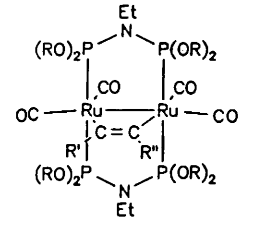
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

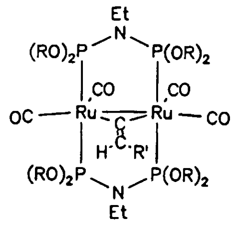
**Table 1** Ratio of the alkenediyl- (**5**) and vinylidene-bridged isomers (**6**) in the product mixture of the reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ with $R'C{\equiv}CR''$

| Reactants[a] | | | Products (%) | |
|---|---|---|---|---|
| R | R′ | R″ | **5** | **6** |
| Me | H | H | 95 | 5 |
| Et | H | H | 70 | 30 |
| $Pr^i$ | H | H | 10 | 90 |
| Me | Me | H | 20 | 80 |
| $Pr^i$ | Me | H | 0 | 100 |
| Me | Ph | H | 0 | 100 |
| $Pr^i$ | Ph | H | 0 | 100 |
| Me | Ph | Ph | No reaction | |
| $Pr^i$ | Ph | Ph | No reaction | |
| Me | MeOC(O) | H | 100 | 0 |
| $Pr^i$ | MeOC(O) | H | 75 | 25 |
| Me | MeOC(O) | MeOC(O) | 100 | 0 |
| $Pr^i$ | MeOC(O) | MeOC(O) | 100 | 0 |

[a] Reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}]$ with $HC{\equiv}CH$ afforded the alkenediyl- and vinylidene-bridged isomers in the ratio 55:45.



| | R | R′ | R″ |
|---|---|---|---|
| **5a** | Me | H | H |
| **5b** | Et | H | H |
| **5c** | $Pr^i$ | H | H |
| **5d** | Me | H | Me |
| **5e** | Me | H | $CO_2Me$ |
| **5f** | $Pr^i$ | H | $CO_2Me$ |
| **5g** | Me | $CO_2Me$ | $CO_2Me$ |
| **5h** | $Pr^i$ | $CO_2Me$ | $CO_2Me$ |



| | R | R′ |
|---|---|---|
| **6a** | Me | H |
| **6b** | Et | H |
| **6c** | $Pr^i$ | H |
| **6d** | Me | Me |
| **6e** | $Pr^i$ | Me |
| **6f** | $Pr^i$ | $CO_2Me$ |
| **6g** | Me | Ph |
| **6h** | $Pr^i$ | Ph |

$(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me **1a** or $Pr^i$ **1c**)[1] with ethyne, in toluene at 80 °C for 1 h, was found to lead to the ready formation of yellow crystalline products, the microanalyses of which were consistent with the formulation $[Ru_2(HC{\equiv}CH)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$. The IR spectra of these products in the C–O stretching region were very similar to those of the corresponding parent complexes, **1a** and **1c** respectively, but with the peak corresponding to the bridging carbonyl ligand in the latter being absent. However, the $^{31}P\text{-}\{^1H\}$ NMR spectra of these species exhibited two singlets, although, in each case, the intensity of the weaker singlet was less than one tenth of that of the stronger peak. It was concluded that two products were formed in each reaction and, on the basis of the $^1H$ and $^{13}C\text{-}\{^1H\}$ NMR spectroscopic evidence, that the major product from the reaction involving the tetramethoxydiphosphazane bridged complex **1a** (Table 1) was the ethenediyl-bridged species $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}_2]$ **5a**; a singlet at δ 7.11, corresponding to two protons, was observed in the proton spectrum while a quintet at δ 121.0 was observed in the $^{13}C\text{-}\{^1H\}$ spectrum. A distortionless enhancement by polarization transfer (DEPT) analysis of the latter indicated that the quintet corresponds to one or more carbon atoms, each containing a single hydrogen atom. The minor product formed in this reaction was identified as the vinylidene-bridged isomer $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CH_2)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}_2]$ **6a** on the basis that a very weak quintet is observed at δ 6.51 in its $^1H$ NMR spectrum and that the analogous tetraisopropoxydiphosphazane-bridged vinylidene-bridged species $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CH_2)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **6c** (see below) likewise exhibits a quintet in this region of its $^1H$ NMR spectrum.

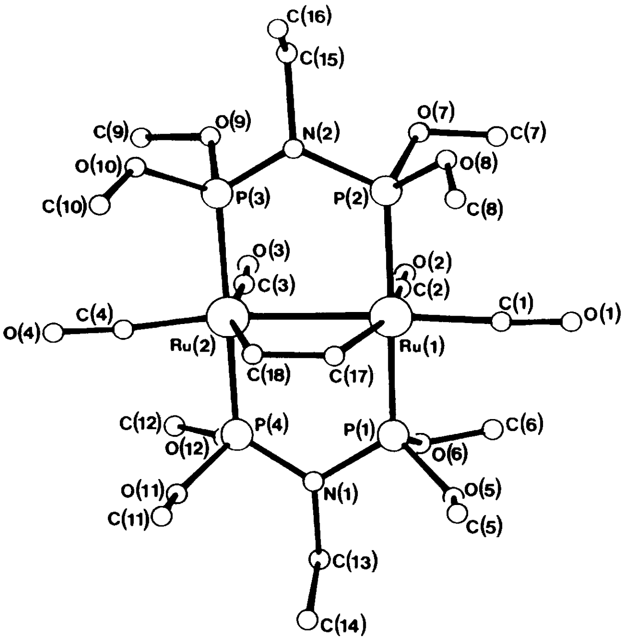


**Fig. 1** Structure of $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}_2]$. Only the molecule situated on a general equivalent position is shown, the other being disordered about a crystallographic centre of symmetry

In contrast to that observed for **1a**, the major product formed in the reaction of the tetraisopropoxydiphosphazane-bridged complex **1c** with ethyne was established to be a vinylidene-bridged species *viz.* $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CH_2)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **6c**; a quintet at δ 6.36, corresponding to two protons, was observed in the $^1H$ NMR spectrum of the product while two quintets at δ 232.7 and δ 131.9 were observed in the $^{13}C\text{-}\{^1H\}$ NMR spectrum. A DEPT analysis of this spectrum revealed that the former quintet corresponds to a quaternary carbon atom while the latter corresponds to a carbon atom containing two protons. These quintets were thus assigned to the α and β carbon atoms respectively of a bridging vinylidene group. The minor product formed in this reaction was identified as the ethenediyl-bridged isomer $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **5c** on the basis of a very weak singlet at δ 7.01 in the $^1H$ NMR spectrum.

The co-ordination of the ethyne in **5a** as an alkenediyl group parallel to the ruthenium–ruthenium vector rather than as a $\eta^2$-alkyne perpendicular to this vector was confirmed by means of an X-ray crystal-structure determination. The stereochemistry of the compound is illustrated in Fig. 1. The compound adopts an eclipsed configuration with a Ru–Ru distance of 2.857(1) Å (average for the two independent molecules in the asymmetric unit) which is slightly longer than that for the parent compound **1a** [2.801(2) Å].[1] The ethenediyl mode of co-ordination of ethyne in **5a** is the same as that established for $PhC{\equiv}CPh$ in the dmpm-bridged diruthenium species $[Ru_2(\mu\text{-}\sigma^2\text{-}PhC{=}CPh)(CO)_4(\mu\text{-}dmpm)_2]$ **4a**.[9]

Consistent with that observed for **1a** and **1c**, the mixed-ligand species $[Ru_2(\mu\text{-}CO)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}]$, containing both the tetramethoxydiphosphazane and the more bulky tetraisopropoxydiphosphazane ligands, was shown to react with ethyne under the above reaction conditions to afford both the ethenediyl- and the vinylidene-bridged isomers, **7** and **8**, in approximately equal yields. This assignment was based on the presence of two AA'BB' patterns of peaks of roughly equal intensity in the $^{31}P-\{^1H\}$ NMR spectrum of the product and a singlet at δ 7.10 and a quintet at δ 6.52, the integrated intensities of which were approximately the same, in the $^1H$ NMR spectrum. In addition, a quintet at δ 121.6, assigned to the carbon atoms of the ethenediyl group in **7**, was observed in the $^{13}C-\{^1H\}$ NMR spectrum as were quintets at δ 235.8 and 132.6, readily assigned to the α and β carbon atoms respectively of the vinylidene group in **8**.

The tetraethoxydiphosphazane-bridged derivative $[Ru_2(\mu-CO)(CO)_4\{(EtO)_2PN(Et)P(OEt)_2\}_2]$ **1b** was also treated with ethyne and in this case the ethenediyl- and vinylidene-bridged isomers, **5b** and **6b** respectively, were found to be formed with a product ratio of 7:3.

(*ii*) *Reaction of* $[Ru_2(\mu-CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ *with the terminal alkynes* R'C≡CH (R' = Me, Ph *or* $MeO_2C$). $[Ru_2(\mu-CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ **1** were also treated with the terminal alkynes methylacetylene, phenylacetylene and methyl propiolate in toluene at 80 °C and again either the alkenediyl- or the vinylidene-bridged isomer or both were found to be formed with the ratio of the isomers in the product mixture being dependent on the alkyne and the bridging diphosphazane ligand, as summarized in Table 1. Thus while the reaction of the tetramethoxydiphosphazane-bridged species **1a** with MeC≡CH afforded both the propenediyl- and methylvinylidene-bridged isomers, **5d** and **6d** respectively, in the approximate ratio 1:4, the reaction of the more bulky tetraisopropoxydiphosphazane-bridged complex **1c** with this alkyne afforded the methylvinylidene-bridged isomer, **6e**, as the sole product.

Consistent with the above trend in terms of the relative yields of the alkenediyl- and vinylidene-bridged isomers, reaction of **1a** and **1c** with PhC≡CH, in refluxing hexane or in toluene at 80 °C, afforded solely the phenylvinylidene species, **6g** and **6h** respectively. In contrast, reaction of **1a** with $MeO_2CC{\equiv}CH$ afforded the alkenediyl-bridged derivative $[Ru_2(\mu-\sigma^2-MeO_2CC{=}CH)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}_2]$ **5e** as the sole product while the corresponding reaction involving the tetraisopropoxydiphosphazane-bridged species, **1c**, produced a mixture of the alkenediyl- and vinylidene-bridged isomers $[Ru_2(\mu-\sigma^2-MeO_2CC{=}CH)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **5f** and $[Ru_2(\mu-\sigma-C{=}CHCO_2Me)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **6f** respectively, in the ratio 3:1. It was possible to separate **5f** from **6f** by fractional crystallization and to isolate it in a pure state and significantly heating this pure sample in toluene under reflux for several hours did not lead to its conversion to the vinylidene-bridged isomer **6f**.

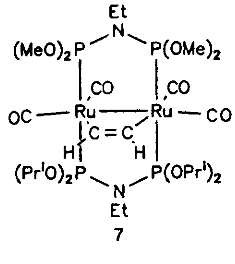
(*iii*) *Reaction of* $[Ru_2(\mu-CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ *with the internal alkynes* R''C≡CR'' (R'' = $MeO_2C$ *or* Ph). Treatment of $[Ru_2(\mu-CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ **1** with dimethyl acetylenedicarboxylate in toluene at 80 °C was found to lead to the sole formation of the alkenediyl-bridged product $[Ru_2(\mu-\sigma^2-MeO_2CC{=}CCO_2Me)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ for both R = Me and $Pr^i$ (**5g** and **5h**). On the other hand no reaction was observed on treatment of **1** with diphenylacetylene under the same reaction conditions. This contrasts with that established for the related, more electron-rich, dmpm-bridged derivative $[Ru_2(\mu-CO)(CO)_4(\mu-dmpm)_2]$ which afforded $[Ru_2(\mu-\sigma^2-PhC{=}CPh)(CO)_4(\mu-dmpm)_2]$ **4b** in high yield as described above.[9]

(*iv*) *Reaction of* $[Ru_2(\mu_{sb}-CO)_2(CO)_2\{(RO)_2PN(Et)P(OR)_2\}_2]$ *with various alkynes.* To assist in elucidating the mechanism of the reactions of compound **1** with alkynes, the corresponding reactions involving the unsaturated species $[Ru_2(\mu_{sb}-CO)_2(CO)_2\{(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me **2a** or $Pr^i$ **2b**)[8] were investigated. Treatment of the latter at room temperature, with the various alkynes described above, was found to lead to a spontaneous reaction and to afford the same products in the same isomeric ratio as the corresponding reactions involving **1**. Thus, while **2a** reacts with ethyne in toluene at room temperature to give the ethenediyl-bridged species **5a** as the major product, compound **2b** reacts with this alkyne under the same reaction conditions to afford the vinylidene-bridged species **6c** as the major product.

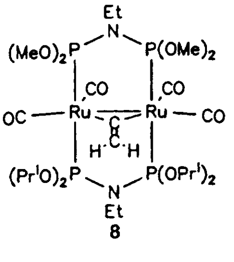
With the object of identifying possible intermediates in the formation of the alkenediyl- and vinylidene-bridged products, the reaction of **2b** with PhC≡CH in $C_6D_6$ was monitored by means of $^1H$ NMR spectroscopy. Triplets at δ −8.06 and δ −8.98 were observed in this spectrum and it is thus apparent that the formation of **6h** occurs via hydridic intermediates. However because of the rapid rate of formation of the final product, it was not possible to establish whether the two hydrides are formed in consecutive or separate steps. The reaction of **2b** with $MeO_2CC{\equiv}CH$ in $C_6D_6$ was also monitored by means of $^1H$ NMR spectroscopy and two triplets, at δ −6.54 and δ −8.00, were again observed. On the other hand hydridic intermediates could not be detected in the monitored reaction of the unsaturated tetramethoxydiphosphazane-bridged species **2a** with $MeO_2CC{\equiv}CH$ in $C_6D_6$. In summary intermediates containing a hydride ligand could be readily detected in the formation of the vinylidene-bridged derivatives but not the alkenediyl-bridged products.

*Mechanism of Reaction.*—The formation of both an alkenediyl- and a vinylidene-bridged product in the same reaction involving a metal substrate and an alkyne is unusual and, as far as the authors are aware, has not been reported previously;[12] Berry and Eisenberg[13] have established that the reaction of $[Rh_2(CO)_3(\mu-dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) with phenylacetylene affords either the phenylvinylidene-bridged complex $[Rh(\mu-\sigma-C{=}CHPh)(CO)_2(\mu-dppm)_2]$ or the $\eta^2$-alkyne-bridged species $[Rh_2(\mu-\eta^2-HC{\equiv}CPh)(CO)_2(\mu-dppm)_2]$, as opposed to the $\sigma^2$-alkenediyl-bridged species, but even then different reaction conditions are required.* The observation that minor modifications to the bridging diphosphazane ligands in the complexes of type **1** can lead to major differences in the relative yields of the alkenediyl- and vinylidene-bridged isomers is equally novel. Werner and co-workers[15–20] have shown previously that mononuclear alkyne complexes of the type $[MCl(\eta^2-HC{\equiv}CR')(PR_3)_2]$ (M = Rh or Ir, R = Me or $Pr^i$, R' = H or Ph) rearrange to the vinylidene isomers $[MCl(C{=}CHR')(PR_3)_2]$ and that the ease of this transformation is dependent not only on the alkyne but on the bulkiness of the phosphine ligand as well,[15–20] but the diruthenium alkenediyl-bridged compounds, **5**, isolated in this study are not intermediates in the formation of the corresponding vinylidene-bridged species, **6** (see above).

A number of features and observations were taken into



**7**



**8**

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* Xiao and Cowie[14] have very recently identified an ethenediyl derivative, $[Ir_2(\mu-\sigma^2-HC{=}CH)I_2(CO)_2(\mu-dppm)_2]$, as an intermediate in the formation of the vinylidene-bridged compound $[Ir(\mu-\sigma-C{=}CH_2)I_2(CO)_2(\mu-dppm)_2]$. However, as a consequence of its rapid rearrangement it was not possible to isolate and fully characterise this intermediate and its identification was on the basis of spectroscopic evidence.

consideration in proposing a mechanism for the formation of the alkenediyl- and vinylidene-bridged derivatives.

(*i*) The formation of both the alkenediyl- and the vinylidene-bridged compounds is irreversible and in particular it was established that passage of carbon monoxide through solutions of these complexes at room- and elevated-temperature does not lead to the formation of the parent diruthenium species **1**.

(*ii*) The reactions involving the unsaturated species **2** afford the same products in the same isomeric ratios as the corresponding reactions involving **1**. This is consistent with the latter reactions occurring *via* a dissociative mechanism.

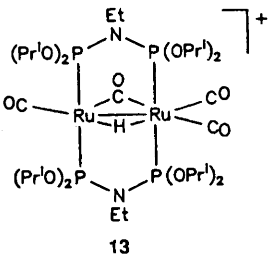
(*iii*) Intermediates in the formation of the alkenediyl-bridged isomers could not be detected on monitoring their formation from both **1** and **2** by means of IR and NMR spectroscopy which is again consistent with a dissociative mechanism for those reactions involving the pentacarbonyl species as precursor. This observation, together with that discussed under (*ii*), is interpreted in terms of products of the type $[Ru_2\{\mu\text{-}\sigma^2\text{-}R'C{=}C(R'')C(O)\}(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ not being formed in the reactions involving **1** or for that matter of the type $[Ru_2\{\mu\text{-}\eta^3\text{-}R'CC(R'')C(O)\}(CO)_3\{(RO)_2PN(Et)P(OR)_2\}_2]$ in those involving both **1** and **2** although the possible formation of the latter cannot be totally eliminated. On the other hand reaction of the related ditertiary phosphine-bridged derivative $[Ru_2(\mu\text{-}CO)(CO)_6(\mu\text{-}dppm)]$ with ethyne has been shown to afford $[Ru_2\{\mu\text{-}\eta^3\text{-}HCC(H)C(O)\}(CO)_5(\mu\text{-}dppm)]$ in which the HCC(H)C(O) group functions as a four-electron donor.[21]

(*iv*) The ratio of the alkenediyl- and vinylidene-bridged isomers formed in any particular reaction is invariant to both the temperature of the reaction and, more importantly, to the reaction time. Furthermore pure $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CCO_2Me)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **5f**, separated from its vinylidene-bridged isomer $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CHCO_2Me)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **6f** by fractional crystallization, could not be converted to the latter even when heated in solution at elevated temperatures. In fact in no cases, irrespective of the alkyne and the diphosphazane ligand, was it possible to convert one isomer into the other. It is thus apparent that the alkenediyl-bridged isomers are *not* intermediates in the formation of the corresponding vinylidene-bridged derivatives and that the two isomers are formed *via* different pathways. This conclusion is consistent with that reached by Silvestre and Hoffmann[22] on the basis of a theoretical analysis of the transformation of dinuclear alkenediyl derivatives to their corresponding vinylidene species. Their extended-Hückel calculations revealed that the transition state for the process was very high in energy and as a consequence they concluded that the process was a highly unlikely one.

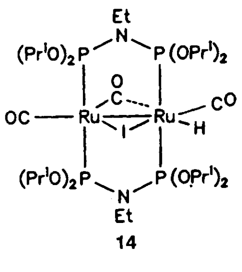
(*v*) As described above, intermediates containing a hydride ligand could be detected in the formation of the vinylidene-bridged isomers and in particular in the formation of $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CHPh)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ and $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CHCO_2Me)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. Two hydridic intermediates were detected in both of the latter reactions but, as also described above, it was not possible to establish whether the two hydrides are formed in consecutive or separate steps because of the rapid rate of formation of the vinylidene-bridged product.

Possible reaction pathways for the formation of the alkenediyl- and the vinylidene-bridged derivatives are illustrated in Scheme 1. Two pathways, both of which involve an intramolecular oxidative addition of the alkyne affording an alkynyl–hydrido intermediate, are considered for the formation of the vinylidene-bridged isomers. Pathway (*ii*)(*a*) considers the transformations to occur at a single ruthenium atom and is analogous to that established by Werner and co-workers[15–20] for the formation of mononuclear vinylidene products in the reaction of a number of rhodium and iridium compounds with terminal alkynes. Knox and co-workers[23] have proposed a related pathway for the reaction of $[Ru_2(cp)_2(\mu\text{-}CO)_2(CO)(MeCN)]$ (cp = $\eta^5\text{-}C_5H_5$) with ethyne to give $[Ru_2\{\mu\text{-}\eta^3\text{-}HCC(H)C(O)\}(cp)_2(\mu\text{-}CO)(CO)]$, the latter subsequently isomerising to $[Ru_2(\mu\text{-}C{=}CH_2)(cp)_2(\mu\text{-}CO)(CO)_2]$. Pathway (*ii*) (*b*), on the other hand, considers the transformations to occur across the two ruthenium atoms. As described above, a product analogous to **11** and containing a $\eta^2$-bridging alkyne ligand *viz.* the ditertiary phosphine-bridged dirhodium derivative $[Rh_2(\mu\text{-}\eta^2\text{-}HC{\equiv}CPh)(CO)_2(\mu\text{-}dppm)_2]$, has been shown to be formed in the reaction of $[Rh_2(CO)_3(\mu\text{-}dppm)_2]$ with phenylacetylene.[13] Also products analogous to **12**, $[Re_2(\mu\text{-}H)(\sigma\text{-}C{\equiv}CR')(CO)_7(\mu\text{-}R_2PCH_2PR_2)]$ (R = Me or Ph, R′ = H or Ph) containing a bridging hydride ligand as well as a terminal alkynyl group, have been isolated from the reactions of $[Re_2(CO)_8(\mu\text{-}R_2PCH_2PR_2)]$ with both ethyne and phenylacetylene;[24] the structure proposed for **12** is based on that established for $[Ru_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_3\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ **13** and $[Ru_2(\mu\text{-}I)H(\mu_{sb}\text{-}CO)(CO)_2\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **14**.[25] However, as also described above, although $[Rh_2(\mu\text{-}\sigma\text{-}C{=}CHPh)(CO)_2(\mu\text{-}dppm)_2]$ is also a product of the reaction of $[Rh_2(CO)_3(\mu\text{-}dppm)_2]$ with phenylacetylene, it is formed *via* a different pathway to the $\eta^2$-alkyne-bridged derivative. Furthermore although the latter can be isomerized to the vinylidene-bridged derivative, the transformation is slow and several days are required even at elevated temperatures (80 °C).[13] Nevertheless Silvestre and Hoffmann[22] have established from their extended-Hückel calculations that dinuclear complexes containing a hydride group co-ordinated to the one metal atom and an alkynyl ligand σ-bonded to the other can be readily transformed to their corresponding vinylidene-bridged products. A similar scheme has been proposed by Xiao and Cowie[14] for the formation of $[Ir_2(\mu\text{-}\sigma\text{-}C{=}CHR')I_2(CO)_2(\mu\text{-}dppm)_2]$ in the reactions of $[Ir_2I_2(\mu\text{-}CO)(CO)(\mu\text{-}dppm)_2]$ with ethyne and phenylacetylene.[14] However these authors concluded that the alkenediyl derivative $[Ir_2(\mu\text{-}\sigma^2\text{-}HC{=}CR')I_2(CO)_2(\mu\text{-}dppm)_2]$ (R′ = H or Ph) is an intermediate in this reaction while furthermore the rearrangement of a second intermediate, identified as $[Ir_2(\mu\text{-}\sigma,\eta^2\text{-}HC{=}CH)I(CO)_2(\mu\text{-}dppm)_2]I$, to the final product in the reaction involving ethyne was found to be slow requiring *ca.* 20 h for full conversion at room temperature. An alternative to **12** as an intermediate in pathway (*ii*) (*b*) is **15** in which the alkynyl ligand bridges the two ruthenium atoms in an open σ,π-co-ordination mode. Examples of compounds with this mode of co-ordination, have been reported previously although all have closed configurations.[26–29]

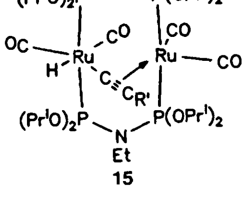
The formation of the alkenediyl-bridged isomers is proposed to occur in a single step, (*i*), and no intermediates are envisaged. Significantly Higgins and Shaw[30,31] have synthesized the dipalladium vinylidene-bridged derivative $[Pd_2(\mu\text{-}\sigma\text{-}C{=}CH_2)$-



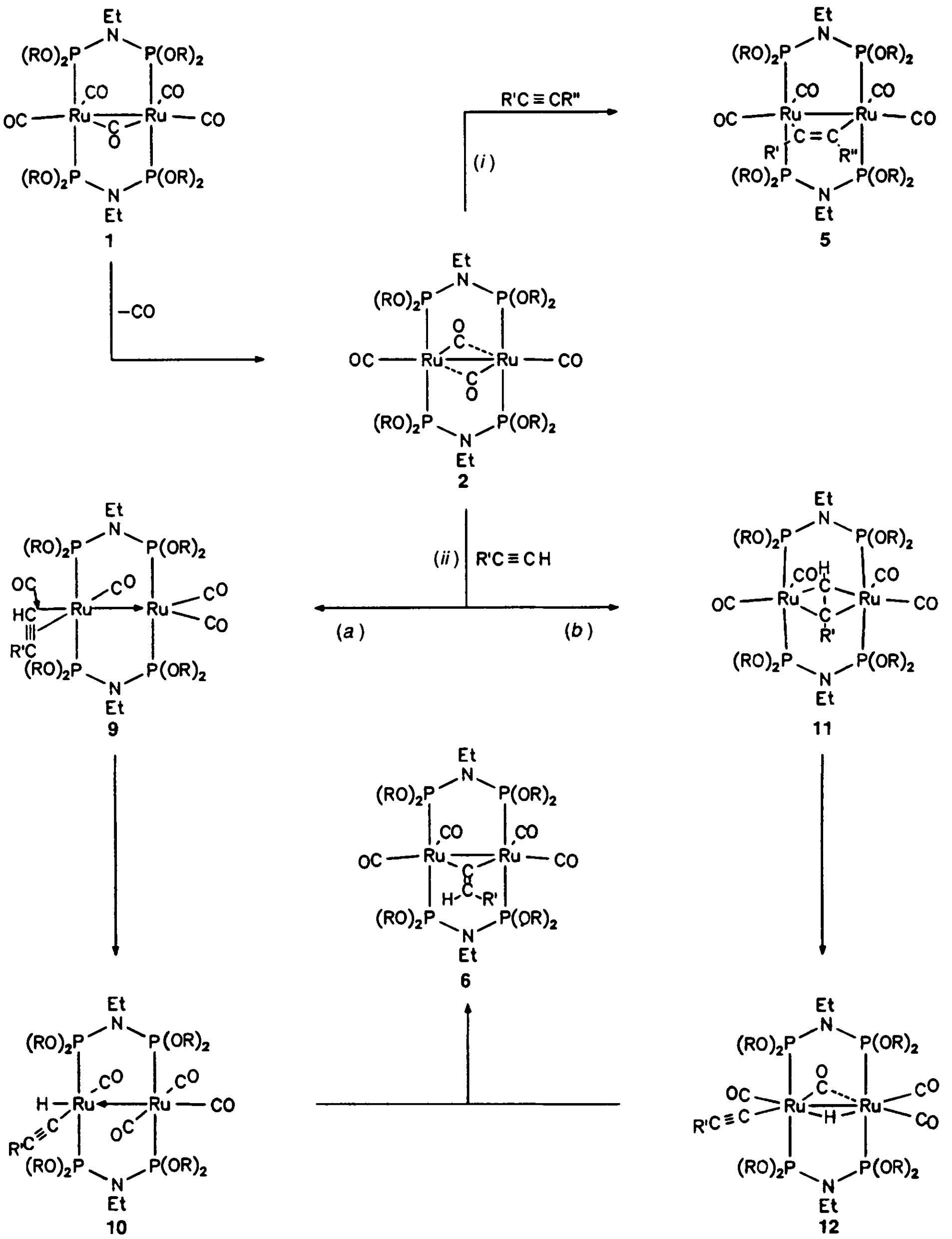
**13**



**14**



**15**



**Scheme 1** Proposed reaction pathways for the formation of alkenediyl- and vinylidene-bridged products in the reactions of $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2}]$ and $[\mathrm{Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{(RO)_2PN(Et)P(OR)_2\}_2}]$ with various alkynes [R = Me or Pr$^i$, R' = H, Me, Ph or C(O)OMe, R″ = H or C(O)OMe]

$\mathrm{Cl_2(\mu\text{-}dppm)_2}]$ as well as its alkenediyl-bridged isomer $[\mathrm{Pd_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)Cl_2(\mu\text{-}dppm)_2}]$, different synthetic methods being required, and established that similarly to the diruthenium vinylidene- and alkenediyl-bridged derivatives discussed above, these isomers are not interconvertible.

## Experimental

The neutral pentacarbonyls $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2}]$ (R = Me, Et or Pr$^i$) and $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}}]$ and tetracarbonyls $[\mathrm{Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{(RO)_2PN(Et)P(OR)_2\}_2}]$ (R = Me or Pr$^i$) were synthesized according to literature methods.[1,8,32] All reactions and manipulations were carried out under an atmosphere of nitrogen by Schlenk techniques. Solvents were purified and dried using standard literature procedures and were degassed prior to use by two freeze-pump-thaw cycles. Infrared spectra were measured on a Perkin Elmer 457 spectrometer. The $^{31}$P-{$^1$H} NMR spectra were recorded on a Varian FT80A instrument while $^{13}$C-{$^1$H} and $^1$H NMR spectra were obtained on a Varian Gemini 200 spectrometer. Spectroscopic data are summarized in Tables 2 and 3.

*Syntheses*.—$[\mathrm{Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2}]$ *and* $[\mathrm{Ru_2(\mu\text{-}\sigma\text{-}C{=}CH_2)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2}]$ (R = Me, Et *or* Pr$^i$). A stream of ethyne was passed slowly through a solution of **1a** (0.30 g, 0.38 mmol), **1b** (0.30 g, 0.33 mmol) or **1c** (0.30 g, 0.29 mmol) in toluene (15 cm$^3$) at 80 °C for 1 h. The yellow solution was cooled to room temperature under a flow of ethyne and then concentrated under reduced pressure to *ca.* 3 cm$^3$. Methanol (5 cm$^3$) was added to the solution to effect the precipitation of the products as yellow microcrystals which were spectroscopically identified as being mixtures of the alkenediyl- and vinylidene-bridged isomers. Yield: 80–95% (Found: C, 27.8; H, 4.5; N, 3.2. $\mathrm{C_{18}H_{36}N_2O_{12}P_4Ru_2}$ requires C, 27.1; H, 4.6; N, 3.5. Found: C, 34.5; H, 5.8; N, 2.8.

**Table 2** Infrared spectroscopic data

| Compound | | ν(CO)$^a$/cm$^{-1}$ |
|---|---|---|
| **5a** | [Ru$_2$(μ-σ$^2$-HC=CH)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]$^b$ | 2001s, 1964vs, 1933s, 1915s$^d$ |
| **6a** | [Ru$_2$(μ-σ-C=CH$_2$)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]$^c$ | |
| **5b** | [Ru$_2$(μ-σ$^2$-HC=CH)(CO)$_4${(EtO)$_2$PN(Et)P(OEt)$_2$}$_2$]$^b$ | 1998s, 1962vs, 1928ms, 1908s$^d$ |
| **6b** | [Ru$_2$(μ-σ-C=CH$_2$)(CO)$_4${(EtO)$_2$PN(Et)P(OEt)$_2$}$_2$]$^c$ | |
| **5c** | [Ru$_2$(μ-σ$^2$-HC=CH)(CO)$_4${(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}$_2$]$^c$ | 1991s, 1947s, 1906s, 1890s$^d$ |
| **6c** | [Ru$_2$(μ-σ-C=CH$_2$)(CO)$_4${(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}$_2$]$^b$ | |
| **5d** | [Ru$_2$(μ-σ$^2$-HC=CMe)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]$^c$ | 1992s, 1953s, 1917s, 1897s$^d$ |
| **6d** | [Ru$_2$(μ-σ-C=CHMe)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]$^b$ | |
| **5e** | [Ru$_2$(μ-σ$^2$-HC=CCO$_2$Me)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$] | 2007s, 1973vs, 1942s, 1923s 1674m$^d$ |
| **5f** | [Ru$_2$(μ-σ$^2$-HC=CCO$_2$Me)(CO)$_4${(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}$_2$]$^b$ | 2000s, 1963vs, 1930ms, 1908s, 1665m$^d$ |
| **6f** | [Ru$_2$(μ-σ-C=CHCO$_2$Me)(CO)$_4${(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}$_2$]$^c$ | |
| **5g** | [Ru$_2$(μ-σ$^2$-MeO$_2$CC=CCO$_2$Me)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$] | 2000s, 1978s, 1949s, 1927ms, 1675ms$^d$ |
| **5h** | [Ru$_2$(μ-σ$^2$-MeO$_2$CC=CCO$_2$Me)(CO)$_4${(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}$_2$] | 2001s, 1967vs, 1940s, 1917s, 1678ms$^d$ |
| **6e** | [Ru$_2$(μ-σ-C=CHMe)(CO)$_4${(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}$_2$] | 1986s, 1943s, 1905s, 1888s$^d$ |
| **6g** | [Ru$_2$(μ-σ-C=CHPh)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$] | 1999s, 1966vs, 1932s, 1914s$^e$ |
| **6h** | [Ru$_2$(μ-σ-C=CHPh)(CO)$_4${(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}$_2$] | 1992vs, 1949vs, 1918s, 1891vs$^e$ |
| **7** | [Ru$_2$(μ-σ$^2$-HC=CH)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}{(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}]$^b$ | 1998s, 1957s, 1923ms, 1907s$^d$ |
| **8** | [Ru$_2$(μ-σ-C=CH$_2$)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}{(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}]$^c$ | |

[a] Abbreviations: v = very, s = strong, m = medium. [b] Major isomer. [c] Minor isomer. [d] Measured in cyclohexane. [e] Measured in CCl$_4$.

**Table 3** $^{31}$P-{$^1$H}, $^1$H and $^{13}$C-{$^1$H} nuclear magnetic resonance spectroscopic data

| Compound | $^{31}$P-{$^1$H}$^a$ | $^1$H$^b$ | $^{13}$C-{$^1$H}$^b$ |
|---|---|---|---|
| **5a**$^c$ | 153.0 (s) | 7.11 (s, HC=CH) | 121.0 (qnt, $\lvert ^2J_{PC} + {}^3J_{P'C}\rvert$ 3.9, HC=CH) |
| **6a**$^d$ | 155.7 (s) | 6.51 (qnt, $^4J_{PH}$ 2.4, C=CH$_2$) | *e* |
| **5b**$^c$ | 147.6 (s) | 7.01 (s, HC=CH) | *e* |
| **6b**$^d$ | 150.5 (s) | 6.36 (qnt, $^4J_{PH}$ 2.4, C=CH$_2$) | *e* |
| **5c**$^d$ | 146.1 (s) | 7.02 (s, HC=CH) | |
| **6c**$^c$ | 148.8 (s) | 6.34 (qnt, $^4J_{PH}$ 2.4, C=CH$_2$) | 131.9 (qnt, $^3J_{PC}$ 4.1, C=*C*H$_2$),<br>232.7 (qnt, $^2J_{PC}$ 16.4, *C*=CH$_2$) |
| **5d**$^d$ | 152.9 (s) | 7.25 (s, *H*C=CMe) | 120.6 (qnt, $\lvert ^2J_{PC} + {}^3J_{P'C}\rvert$ 3.8, H*C*=CMe),<br>132.5 (qnt, $\lvert ^2J_{PC} + {}^3J_{P'C}\rvert$ 3.9, HC=*C*Me) |
| **6d**$^c$ | 155.5 (AA′BB′) | 6.43–6.61 (m, C=C*H*Me) | 136.0 (qnt, $^3J_{PC}$ 4.1, C=*C*HMe)<br>223.8 (qnt, $^2J_{PC}$ 16.0, *C*=CHMe) |
| **5e** | 151.6 (AA′BB′) | 9.08 (s, *H*C=CCO$_2$Me) | *e* |
| **5f**$^c$ | 148.0 (AA′BB′) | 9.12 (s, *H*C=CCO$_2$Me) | *e* |
| **6f**$^d$ | 144.1 (AA′BB′) | 7.35 (s, C=C*H*CO$_2$Me) | *e* |
| **5g** | 148.5 (s) | | 146.9 (qnt, $\lvert ^2J_{PC} + {}^3J_{P'C}\rvert$ 4.1, MeO$_2$C*C*=*C*CO$_2$Me) |
| **5h** | 140.9 (s) | | 152.0 (qnt, $\lvert ^2J_{PC} + {}^3J_{P'C}\rvert$ 3.6, MeO$_2$C*C*=*C*CO$_2$Me) |
| **6e** | 148.4 (AA′BB′) | 6.20–6.34 (m, C=C*H*Me) | 134.6 (qnt, $^3J_{PC}$ 4.6, C=*C*HMe),<br>221.8 (qnt, $^2J_{PC}$ 16.2, *C*=CHMe) |
| **6g**$^f$ | 153.9 (s)$^g$ | 8.19 (qnt, $^4J_{PH}$ 2.4, C=C*H*Ph) | *e* |
| **6h** | 146.2 (AA′BB′)$^h$ | 8.23 (qnt, $^4J_{PH}$ 2.4, C=C*H*Ph) | 145.4 (qnt, $^3J_{PC}$ 4.6, C=*C*Ph),<br>234.4 (qnt, $^2J_{PC}$ 15.9, *C*=CHPh) |
| **7** | 147.6 (AA′BB′) | 7.10 (s, HC=CH) | 121.6 (qnt, $\lvert ^2J_{PC} + {}^3J_{P'C}\rvert$ 3.6, HC=CH)$^g$ |
| **8** | 150.5 (AA′BB′) | 6.52 (qnt, $^4J_{PH}$ 2.4, C=CH$_2$)$^h$ | 132.6 (qnt, $^3J_{PC}$ 4.0, C=*C*H$_2$),<br>235.8 (qnt, $^2J_{PC}$ 16.0, *C*=CH$_2$) |

[a] Abbreviations: s = singlet, AA′BB′ = midpoint of AA′BB′ pattern, br = broad, δ scale in ppm, relative to 85% H$_3$PO$_4$; measured in CDCl$_3$ unless otherwise stated. [b] Abbreviations: s = singlet, qnt = quintet, m = multiplet, w = weak, δ scale in ppm; measured in CDCl$_3$ unless otherwise stated, *J* in Hz. [c] Major isomer. [d] Minor isomer. [e] Not measured. [f] Field-desorption mass spectrum: *m/z* 876. [g] Measured in C$_6$D$_6$. [h] Measured in CD$_2$Cl$_2$.

C$_{26}$H$_{52}$N$_2$O$_{12}$P$_4$Ru$_2$ requires C, 34.3; H, 5.8; N, 3.1. Found: C, 39.9; H, 6.6; N, 2.5. C$_{34}$H$_{68}$N$_2$O$_{12}$P$_4$Ru$_2$ requires C, 39.9; H, 6.7; N, 2.7%).

[Ru$_2$(μ-σ$^2$-HC=CH)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}{(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}] *and* [Ru$_2$(μ-σ-C=CH$_2$)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}{(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}]. A stream of ethyne was passed slowly through a solution of [Ru$_2$(μ-CO)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}{(Pr$^i$O)$_2$PN(Et)P(OPr$^i$)$_2$}] (0.30 g, 0.33 mmol) in toluene (15 cm$^3$) at 80 °C for 1 h. The yellow solution was cooled to room temperature under a flow of ethyne and then concentrated under reduced pressure to *ca.* 3 cm$^3$. Crystallization of the isomeric mixture of the title compound was effected by the addition of methanol (5 cm$^3$) to the solution. Yield: 85% (Found: C, 34.5; H, 5.9; N, 2.8. C$_{26}$H$_{52}$N$_2$O$_{12}$P$_4$Ru$_2$ requires C, 34.3; H, 5.8; N, 3.1%).

[Ru$_2$(μ-σ$^2$-HC=CMe)(CO)$_4${(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$] *and* [Ru$_2$(μ-σ-C=CHMe)(CO)$_4${(RO)$_2$PN(Et)P(OR)$_2$}$_2$] (R = Me *or* Pr$^i$). A stream of propyne was passed slowly through a solution of **1a** (0.20 g, 0.25 mmol) or **1c** (0.20 g, 0.20 mmol) in toluene (15 cm$^3$) at 80 °C for 1 h. The yellow solution was cooled to room temperature under a flow of propyne and then concentrated under reduced pressure to *ca.* 3 cm$^3$. Crystallization of the product(s) was effected by the addition of methanol (5 cm$^3$) to the solution, which was then set aside at −10 °C for 15 h. Yield: 80–90% (Found: C, 28.5; H, 4.9; N, 3.4. C$_{19}$H$_{38}$N$_2$O$_{12}$P$_4$Ru$_2$ requires C, 28.1; H, 4.7; N, 3.5. Found: C, 41.5; H, 6.8; N, 2.7. C$_{35}$H$_{70}$N$_2$O$_{12}$P$_4$Ru$_2$ requires C, 40.5; H, 6.8; N, 2.7%).

[Ru$_2$(μ-σ-C=CHPh)(CO)$_4${(RO)$_2$PN(Et)P(OR)$_2$}$_2$] (R = Me *or* Pr$^i$). A slight excess of phenylacetylene (0.06 g, 0.59

**Table 4** Fractional co-ordinates ( × $10^4$) for $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}_2]$

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Ru(1A) | 475(1) | 1864(1) | 4809(1) |
| Ru(2A) | −2325(1) | 1524(1) | 4680(1) |
| P(1A) | 193(2) | 2111(1) | 3633(1) |
| P(2A) | 799(2) | 1545(1) | 5951(1) |
| P(3A) | −1995(2) | 1223(1) | 5831(1) |
| P(4A) | −2570(2) | 1761(1) | 3498(1) |
| O(1A) | 3511(7) | 2030(3) | 4875(4) |
| O(2A) | −226(8) | 2984(3) | 5241(4) |
| O(3A) | −3284(7) | 2605(3) | 5167(4) |
| O(4A) | −5034(7) | 942(3) | 4416(4) |
| O(5A) | 1374(6) | 1963(3) | 3164(3) |
| O(6A) | 178(7) | 2752(3) | 3474(3) |
| O(7A) | 1026(6) | 1975(3) | 6586(3) |
| O(8A) | 2165(5) | 1202(3) | 6187(3) |
| O(9A) | −2652(7) | 1573(3) | 6423(3) |
| O(10A) | −2656(7) | 669(3) | 6008(4) |
| O(11A) | −3325(7) | 1350(4) | 2937(3) |
| O(12A) | −3518(7) | 2288(3) | 3279(4) |
| N(1A) | −1210(7) | 1931(3) | 3106(4) |
| N(2A) | −426(7) | 1170(3) | 6249(3) |
| C(1A) | 2377(9) | 1944(4) | 4838(4) |
| C(2A) | 20(9) | 2563(4) | 5093(5) |
| C(3A) | −2938(9) | 2200(4) | 4973(5) |
| C(4A) | −3989(10) | 1161(4) | 4504(4) |
| C(5A) | 1933(13) | 1431(5) | 3147(6) |
| C(6A) | 1354(12) | 3058(4) | 3663(6) |
| C(7A) | 2167(10) | 2336(4) | 6638(5) |
| C(8A) | 2622(10) | 783(4) | 5754(5) |
| C(9A) | −4089(11) | 1643(6) | 6405(7) |
| C(10A) | −2605(15) | 203(5) | 5558(6) |
| C(11A) | −2909(14) | 799(5) | 2899(7) |
| C(12A) | −4887(13) | 2307(6) | 3377(7) |
| C(13A) | −1406(12) | 2101(6) | 2320(5) |
| C(14A) | −1093(18) | 1701(8) | 1871(7) |
| C(15A) | −187(12) | 935(5) | 7004(5) |
| C(16A) | 320(14) | 373(5) | 7024(7) |
| C(17A) | 273(10) | 1051(4) | 4459(4) |
| C(18A) | −1006(9) | 888(4) | 4411(4) |
| Ru(B) | 4710(1) | 544(1) | −168(1) |
| P(1B) | 3669(3) | 627(1) | 843(2) |
| P(2B) | 5885(4) | 477(1) | −1138(2) |
| O(1B) | 4103(10) | 1685(4) | −525(6) |
| O(2B1) | 7683(17) | 913(6) | 703(9) |
| O(2B2) | 8256(18) | −261(7) | 1076(9) |
| O(3B) | 4399(9) | 1032(3) | 1458(4) |
| O(4B) | 2256(10) | 926(4) | 783(6) |
| O(5B) | 5119(20) | 680(6) | −1873(5) |
| O(6B) | 7332(16) | 821(5) | −1119(7) |
| N(B) | 3478(9) | 87(3) | 1343(5) |
| C(1B) | 4319(11) | 1253(5) | −380(6) |
| C(2B1) | 6704(22) | 788(9) | 400(11) |
| C(2B2) | 7277(23) | −375(9) | 723(12) |
| C(3B) | 4669(16) | 1566(5) | 1302(7) |
| C(4B) | 1080(16) | 700(8) | 349(11) |
| C(5B) | 3856(15) | 844(8) | −2089(7) |
| C(6B) | 7621(16) | 1291(8) | −934(11) |
| C(7B) | 2657(17) | 139(6) | 1997(10) |
| C(8B) | 3574(21) | 235(8) | 2688(9) |
| C(9B1) | 6307(19) | 454(9) | 551(10) |
| C(9B2) | 6549(19) | −25(8) | 672(10) |

mmol) was added to a solution of **1a** (0.40 g, 0.49 mmol) or **1c** (0.50 g, 0.50 mmol) in *n*-hexane (50 $cm^3$) and the solution refluxed for 2 h. The initial orange-red colour gradually turned yellow. The volume of the reaction mixture was concentrated under reduced pressure to *ca.* 10 $cm^3$ and kept at 0 °C for 15 h. The yellow microcrystalline product which separated was washed with cold hexane (5 $cm^3$, −20 °C). Yield: 80–85% (Found: C, 33.5; H, 4.8; N, 3.1. $C_{24}H_{40}N_2O_{12}P_4Ru_2$ requires C, 33.0; H, 4.6; N, 3.2. Found: C, 43.6; H, 6.6; N, 2.5. $C_{40}H_{72}N_2O_{12}P_4Ru_2$ requires C, 43.7; H, 6.6; N, 2.5%).

$[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CCO_2Me)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me *or* $Pr^i$) *and* $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CHCO_2Me)(CO)_4\{(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. A solution of a slight excess of methyl propiolate (0.02 g, 0.27 mmol) and **1a** (0.20 g, 0.25 mmol) or **1c** (0.25 g, 0.24 mmol) in toluene (15 $cm^3$) was heated at 80 °C for 1 h. All volatiles were removed under reduced pressure and the yellow oil which remained was washed with cold methanol (3 × 3 $cm^3$, −10 °C). The solid residue remaining was dissolved in toluene (3 $cm^3$), methanol (5 $cm^3$) was added and the solution set aside at −10 °C for 15 h. The yellow microcrystalline product which separated was washed with cold methanol (3 $cm^3$, −10 °C) and dried under vacuum. Yield: 75–85% (Found: C, 28.1; H, 4.5; N, 3.2. $C_{20}H_{38}N_2O_{12}P_4Ru_2$ requires C, 28.0; H, 4.5; N, 3.3. Found: C, 39.3; H, 6.5; N, 2.9. $C_{36}H_{70}N_2O_{14}P_4Ru_2$ requires C, 40.0; H, 6.5; N, 2.6%).

$[Ru_2(\mu\text{-}\sigma^2\text{-}MeO_2CC{=}CCO_2Me)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me *or* $Pr^i$). A solution of a slight excess of dimethyl acetylenedicarboxylate (0.04 g, 0.28 mmol) and **1a** (0.20 g, 0.25 mmol) or **1c** (0.28 g, 0.27 mmol) in toluene (15 $cm^3$) was heated at 80 °C for 1 h. All volatiles were removed under reduced pressure and the yellow solid which remained was washed with cold methanol (3 × 3 $cm^3$, −10 °C). The solid residue remaining was dissolved in toluene (3 $cm^3$) and crystallization of the compounds as pale yellow crystals was achieved by addition of methanol (5 $cm^3$) and setting aside at −10 °C. Yield: 80–90% (Found: C, 28.8; H, 4.4; N, 3.1. $C_{22}H_{40}N_2O_{16}P_4Ru_2$ requires C, 28.9; H, 4.4; N, 3.1. Found: C, 40.0; H, 6.3; N, 2.1. $C_{38}H_{72}N_2O_{16}P_4Ru_2$ requires C, 40.1; H, 6.4; N, 2.5%).

*Reactions of* $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me *or* $Pr^i$). *With ethyne.* A stream of ethyne was passed slowly through a solution of **2a** (0.10 g, 0.13 mmol) or **2b** (0.10 g, 0.10 mmol) in toluene (5 $cm^3$) for 2 min at room temperature, during which time the solution changed from purple to yellow. The solvent was removed under reduced pressure and the residue identified by means of $^{31}P\text{-}\{^1H\}$ NMR and IR spectroscopy as being a mixture of the vinylidene-bridged derivative $[Ru_2(\mu\text{-}\sigma\text{-}C{=}CH_2)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ and of the alkenediyl-bridged species $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{(RO)_2PN(Et)P(OR)_2\}_2]$ and of approximately the same isomeric ratio as that found for the reaction of the corresponding pentacarbonyl species **1a** or **1c** with ethyne at elevated temperatures.

*With phenylacetylene and dimethyl acetylenedicarboxylate.* A slight excess of $PhC{\equiv}CH$ (0.01 g, 0.11 mmol) or $MeO_2CC{\equiv}CCO_2Me$ (0.02 g, 0.11 mmol) was added to a stirred solution of **2a** (0.08 g, 0.10 mmol) or **2b** (0.10 g, 0.10 mmol) in toluene (5 $cm^3$) at room temperature, resulting in an immediate change in colour of the solution from purple to yellow. The solvent was removed under reduced pressure and the residue remaining was identified by means of $^{31}P\text{-}\{^1H\}$ NMR and IR spectroscopy as being the same as that formed in the reaction of **1a** or **1c** (R = Me or $Pr^i$) with the corresponding alkyne at elevated temperatures.

*Crystal Structure Determination of* $[Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}_2]$.—*Crystal data.* $C_{18}H_{36}N_2O_{12}P_4Ru_2$, *M* = 798.6, yellow crystal of dimensions 0.35 × 0.35 × 0.27 mm, monoclinic, space group $P2_1/c$, $a = 9.844(6)$, $b = 25.126(4)$, $c = 18.914(3)$ Å, $\beta = 96.89(4)°$, $U = 4644.3$ Å$^3$, $Z = 6$, $D_c = 1.71$ g $cm^{-3}$, $\mu$(Mo-K$\alpha$) = 12.13 $cm^{-1}$, $F(000) = 2412$.

**Table 5** Selected interatomic distances (Å) and angles for $[Ru_2(\mu\text{-}\sigma^2\text{-}CH{=}CH)(CO)_4\{(MeO)_2PN(Et)P(OMe)_2\}_2]$

| | | | |
|---|---|---|---|
| Molecule A[a] | | | |
| Ru(1A)–Ru(2A) | 2.867(1) | Ru(1A)–P(1A) | 2.293(3) |
| Ru(1A)–P(2A) | 2.291(2) | Ru(2A)–P(3A) | 2.291(3) |
| Ru(2A)–P(4A) | 2.297(3) | Ru(1A)–C(17A) | 2.148(9) |
| Ru(2A)–C(18A) | 2.158(9) | C(17A)–C(18A) | 1.317(13) |
| Ru(2A)–Ru(1A)–P(1A) | 89.7(1) | Ru(1A)–Ru(2A)–P(3A) | 89.6(1) |
| Ru(2A)–Ru(1A)–P(2A) | 90.0(1) | Ru(1A)–Ru(2A)–P(4A) | 89.6(1) |
| Ru(2A)–Ru(1A)–C(1A) | 168.4(3) | Ru(1A)–Ru(2A)–C(3A) | 92.6(3) |
| Ru(2A)–Ru(1A)–C(2A) | 92.4(3) | Ru(1A)–Ru(2A)–C(4A) | 166.7(3) |
| Ru(2A)–Ru(1A)–C(17A) | 68.8(3) | Ru(1A)–Ru(2A)–C(18A) | 69.0(3) |
| P(1A)–Ru(1A)–P(2A) | 175.1(1) | P(3A)–Ru(2A)–P(4A) | 175.1(1) |
| P(1A)–Ru(1A)–C(1A) | 90.3(3) | P(3A)–Ru(2A)–C(3A) | 91.8(3) |
| P(1A)–Ru(1A)–C(2A) | 91.1(3) | P(3A)–Ru(2A)–C(4A) | 91.7(3) |
| P(1A)–Ru(1A)–C(17A) | 87.9(3) | P(3A)–Ru(2A)–C(18A) | 87.6(2) |
| P(2A)–Ru(1A)–C(1A) | 89.0(3) | P(4A)–Ru(2A)–C(3A) | 93.0(3) |
| P(2A)–Ru(1A)–C(2A) | 92.4(3) | P(4A)–Ru(2A)–C(4A) | 88.0(3) |
| P(2A)–Ru(1A)–C(17A) | 87.4(2) | P(4A)–Ru(2A)–C(18A) | 87.6(2) |
| C(1A)–Ru(1A)–C(2A) | 99.2(4) | C(3A)–Ru(2A)–C(4A) | 100.7(4) |
| C(1A)–Ru(1A)–C(17A) | 99.5(4) | C(3A)–Ru(2A)–C(18A) | 161.6(4) |
| C(2A)–Ru(1A)–C(17A) | 161.2(4) | C(4A)–Ru(2A)–C(18A) | 97.8(4) |
| Ru(1A)–C(17A)–C(18A) | 111.7(7) | Ru(2A)–C(18A)–C(17A) | 110.5(7) |
| Molecule B[b] | | | |
| Ru(B)–Ru(B′) | 2.848(2) | Ru(B)–P(1B) | 2.285(4) |
| Ru(B)–P(2B) | 2.290(4) | Ru(B)–C(2B1) | 2.21(2) |
| Ru(B′)–C(2B2) | 2.15(2) | Ru(B) – C(9B1) | 1.96(2) |
| Ru(B′)–C(9B2) | 1.97(2) | C(9B1)–C(9B2) | 1.24(2) |
| Ru(B′)–Ru(B)–P(1B) | 90.1(1) | Ru(B′)–Ru(B)–P(2B) | 89.9(1) |
| Ru(B′)–Ru(B)–C(1B) | 179.4(4) | Ru(B′)–Ru(B)–C(2B1) | 90.6(6) |
| Ru(B′)–Ru(B)–C(9B1) | 67.1(7) | P(1B)–Ru(B)–P(2B) | 176.3(1) |
| P(1B)–Ru(B)–C(1B) | 89.5(4) | P(1B)–Ru(B)–C(2B1) | 91.7(6) |
| P(1B)–Ru(B)–C(9B1) | 80.4(6) | P(2B)–Ru(B)–C(1B) | 90.5(4) |
| P(2B)–Ru(B)–C(2B1) | 84.6(6) | P(2B)–Ru(B)–C(9B1) | 96.1(6) |
| C(1B)–Ru(B)–C(2B1) | 89.3(7) | C(1B)–Ru(B)–C(9B1) | 112.8(7) |
| C(9B1)–Ru(B)–C(2B2′) | 157.4(8) | | |

[a] Situated on a general equivalent position. [b] Situated on a crystallographic centre of symmetry midway between the Ru atoms. The atoms of the co-ordinated ethyne group and of the two carbonyl ligand *trans* to it are disordered; see Experimental section.

Intensity data were collected on a Nonius CAD-4 diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.710 69 Å). A least-squares fit of high-angle reflections ($\theta > 12°$) was used to obtain accurate cell constants. Diffraction intensities were measured in the range $3 \leqslant \theta \leqslant 23°$ using the $\omega$–2$\theta$ scan technique, with background counts made for half the total scan time on each side of the peak. Three standard reflections, measured every hour, showed a decrease in intensity of 5% on completion of the intensity data collection, a linear decay correction being applied. Absorption corrections were made using the semi-empirical $\psi$-scan method. Of the 5889 unique reflections, 5073 were classed as observed $[I > 3\sigma(I)]$ and these were used for the solution and refinement of the structure. The ruthenium and phosphorus atoms were located using the direct methods routine of the program SHELX 76.[33] Subsequent Fourier syntheses gave the positions of the remaining non-hydrogen atoms. There are two crystallographically independent molecules in the asymmetric unit, one located on a general equivalent position and the other on a centre of symmetry midway between the ruthenium atoms. The atoms of the co-ordinated ethyne and of the two carbonyl groups *trans* to it (the carbonyls *cis* to the Ru–Ru bond) are disordered. Careful examination of electron-density difference maps indicated that the sites *cis* to the Ru–Ru bond and in the equatorial plane are shared equally by the ethyne and carbonyl ligands such that the centre of symmetry is preserved for the crystal as a whole. Accordingly the relevant atoms [C(2B1), C(2B2), O(2B1), O(2B2), C(9B1), C(9B2)] were assigned fixed site occupation factors of 0.5. All the non-hydrogen atoms were assigned anisotropic thermal parameters except for the disordered atoms listed above which were assigned isotropic thermal factors. Hydrogen atoms were not located. A final full-matrix least-squares refinement using the weighting scheme $1/[\sigma^2(F) + 0.0002F^2]$ gave $R$ and $R'$ values of 0.054 and 0.059 (511 parameters) respectively. The maximum absolute shift/e.s.d. in the last least-squares cycle was 0.046 and the largest peak in the final difference Fourier map was 1.39 e Å$^{-3}$. Fractional atomic coordinates are listed in Table 4 and selected interatomic distances and angles are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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