A Series of Rhodium(I) Complexes, including Carbene, Vinylidene and Allenylidene Derivatives, with the Bifunctional Arsine $Pr^i_2AsCH_2CH_2OMe$ as Ligand†

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A series of rhodium(I) complexes containing the new bifunctional arsine ligand $Pr^i_2AsCH_2CH_2OMe$ **I** has been prepared. Most of the compounds were obtained from the ethene derivative *trans*-$\{RhCl(C_2H_4)(Pr^i_2AsCH_2CH_2OMe)_2\}$ **5** which was obtained from $[\{RhCl(C_2H_4)_2\}_2]$ and **I** in about 80% yield. The ethene can be displaced by CO, $CNBu^t$, $CH_2{=}CHC(O)Me$, $CH_2{=}CHCO_2Me$, HC≡CPh, HC≡CCO_2Me, PhC≡$CSiMe_3$, MeC≡CMe, PhC≡CMe, MeC≡CC≡CMe or $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (L) to give the four-co-ordinated rhodium(I) complexes *trans*-$[RhCl(L)(Pr^i_2AsCH_2CH_2OMe)_2]$ almost quantitatively. The reaction of **5** with H_2 affords the dihydride $\{RhH_2Cl(Pr^i_2AsCH_2CH_2OMe)_2\}$ which appears to be fluxional in solution. Photolysis of **5** leads to the elimination of $CH_2{=}CHOMe$ and the formation of *trans*-$[RhCl(C_2H_4)(HAsPr^i_2)_2]$ which is also accessible from **3** and $HAsPr^i_2$. The vinylidene complexes *trans*-$[RhCl(=C{=}CHR)(Pr^i_2AsCH_2CH_2OMe)_2]$ are obtained either on photochemically induced rearrangement of the isomeric alk-1-yne derivatives (R = Ph or CO_2Me) or directly from **5** and HC≡CR (R = Me or Bu^t). The reaction of **5** with a large excess of HC≡CMe or MeC≡CBu^t gives the rhodium(I) allenes *trans*-$[RhCl(CH_2{=}C{=}CHR)(Pr^i_2AsCH_2CH_2OMe)_2]$ (R = H or Bu^t). The allenylidene compounds *trans*-$[RhCl(=C{=}C{=}CRR')(Pr^i_2AsCH_2CH_2OMe)_2]$ (R = Ph, R' = Ph or C_6H_4Me-*o*) are obtained from the functionalized vinylidene derivatives *trans*-$[RhCl(=C{=}CHCRR'OH)(Pr^i_2AsCH_2CH_2OMe)_2]$ upon treatment with Al_2O_3. From *trans*-$[RhCl(=C{=}C{=}CRR')(Pr^i_2AsCH_2CH_2OMe)_2]$ and NaC_5H_5 the half-sandwiches $[C_5H_5Rh(=C{=}C{=}CRR')(Pr^i_2AsCH_2CH_2OMe)]$ have been prepared. Compound **5** reacts with N_2CPh_2 and $N_2C(C_6H_4Me\text{-}p)_2$ to yield the carbene complexes *trans*-$[RhCl(=CR_2)(Pr^i_2AsCH_2CH_2OMe)_2]$ whereas from **5** and $N_2CRC(O)Ph$ (R = H or Ph) the diazoalkane rhodium compounds *trans*-$[RhCl\{N_2CRC(O)Ph\}(Pr^i_2AsCH_2CH_2OMe)_2]$ are obtained.

Our recent interest in the chemistry of transition-metal (Rh,[2] Ir,[3] Ru,[4] Os[5]) complexes containing various phosphinoethers as ligands,[2-5] has prompted us to find out whether arsinoethers have similar co-ordinating properties. As has already been shown by Jeffrey and Rauchfuss,[6] Braunstein and co-workers,[7] Lindner and Bader[8] and others, phosphine derivatives of the general type $R_2P(CH_2)_nY$ (Y = OMe, NMe_2, CO_2Me, *etc.*) behave as hemilabile chelating ligands and, with the support of the weak M–Y bond, are able temporarily to protect a vacant co-ordination site. After cleavage of the M–Y bond, a reactive substrate (*e.g.*, H_2, CO, C_2H_4, C_2H_2, *etc.*) can enter into the co-ordination sphere and, with the metal–ligand moiety acting as a template, may be transformed into a new product. It is therefore not surprising that several complexes with bifunctional phosphines $R_2P(CH_2)_nY$ as ligands are catalytically active species.

Since in our work with phosphinoethers, the compound $Pr^i_2PCH_2CH_2OMe$ has proved to be the most versatile ligand in stabilizing d^6 and d^8 metal centres, we attempted to prepare the corresponding arsine $Pr^i_2AsCH_2CH_2OMe$ by an analogous route. This paper describes the synthesis of the new ligand as well as that of a series of rhodium(I) complexes $[RhCl(L)(Pr^i_2AsCH_2CH_2OMe)_2]$ including those in which L is a carbene, vinylidene or allenylidene unit.

Results and Discussion

Preparation of the Arsinoether.—Since $Pr^i_2PCH_2CH_2OMe$ is accessible from $HPPr^i_2$,[2a] the dialkylarsane $HAsPr^i_2$ (which is prepared from Pr^i_2AsCl and $LiAlH_4$[9]) has been used as starting material for the synthesis of $Pr^i_2AsCH_2CH_2OMe$ **I**. Metallation of $HAsPr^i_2$ with $LiBu^n$ yields the lithiated derivative $LiAsPr^i_2$ which reacts with $ClCH_2CH_2OMe$ *in situ* to give **I** in about 70–75% yield [equation (1)]. At room

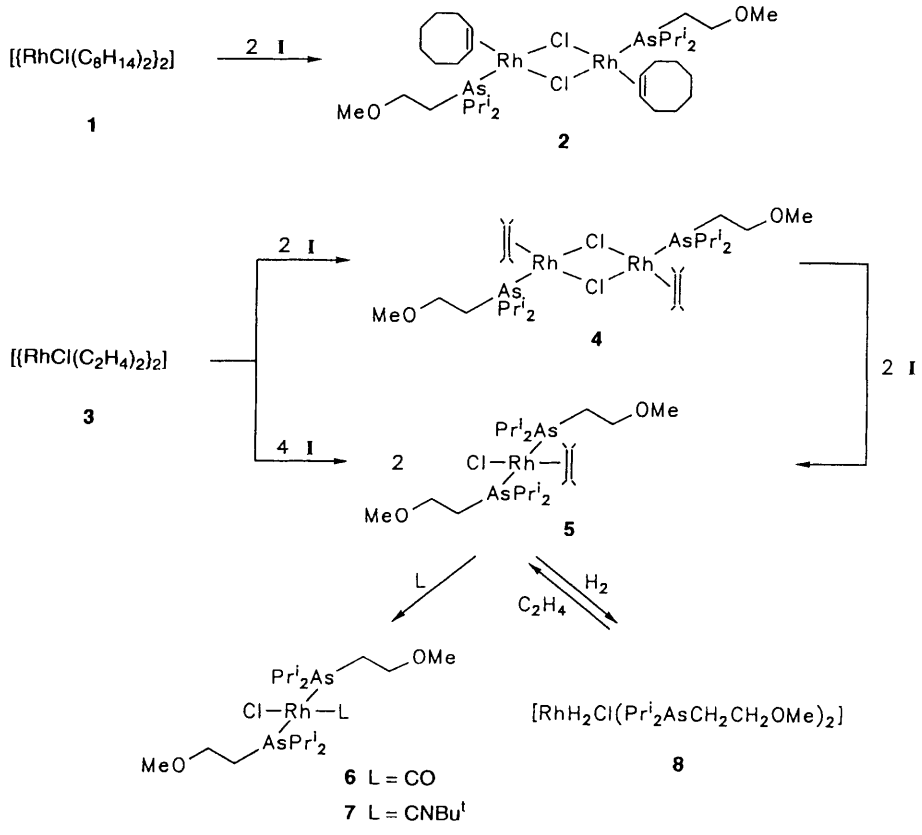
$$HAsPr^i_2 \xrightarrow[(ii)\ ClCH_2CH_2OMe]{(i)\ LiBu^n} \underset{\mathbf{I}}{Pr^i_2AsCH_2CH_2OMe} \quad (1)$$

temperature, the arsinoether is a colourless, extremely air-sensitive liquid which is soluble in all common organic solvents. Due to its sensitivity the adduct of **I** with methyl iodide instead of the free arsine has been characterized by elemental analysis. The ^1H NMR spectrum of **I** displays, besides the singlet for the OCH_3 hydrogens, two doublets for the protons of the diastereotopic methyl groups of the isopropyl units, one septet for the two equivalent AsCH protons and two unresolved multiplets for the hydrogen nuclei of the CH_2CH_2 bridge. The inequivalence of the methyl groups is also illustrated by the ^{13}C NMR spectrum in which two signals are observed for the $AsCHCH_3$ carbons.

Carbonyl, Isocyanide, Hydrido and Olefin Complexes with $[RhCl(Pr^i_2AsCH_2CH_2OMe)_2]$ *as Molecular Unit.*—The bis(cyclooctene)rhodium(I) compound $[\{RhCl(C_8H_{14})_2\}_2]$ **1**, which on treatment with $Pr^i_2PCH_2CH_2OMe$ affords the monomeric substitution product $[RhCl(Pr^i_2PCH_2CH_2OMe)_2]$,[2a] unexpectedly reacts with **I** to give the dimeric complex **2** (see Scheme 1). Even an excess of the arsinoether leads to the same result. In contrast, the course of the reaction of the bis(ethene)rhodium(I) compound $[\{RhCl(C_2H_4)_2\}_2]$ **3** with **I** is strongly dependent on the amount of the arsinoether added. Whereas from **3** and two equivalents of **I**, the chloro-bridged

† Vinylidene Transition-metal Complexes. Part 33.[1]

Non-SI unit employed: Torr ≈ 133 Pa.



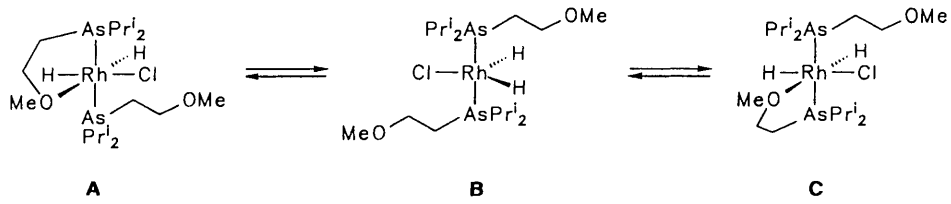
Scheme 1

dimer **4** is formed in excellent yield, only the monomeric product **5** is obtained on reaction with four equivalents (or an excess) of **I**. The obvious assumption that **4** is an intermediate in the formation of **5** has been substantiated by treatment of **4** with 2–3 equivalents of **I** which gives the bis(arsinoether) complex almost quantitatively. The three products, **2**, **4** and **5**, are orange to orange-yellow crystalline solids for which correct elemental analyses have been obtained. The ^{1}H NMR spectrum of complex **5** which displays two doublets for the AsCHCH_3 protons leaves no doubt that the arsine ligands are in *trans* disposition.

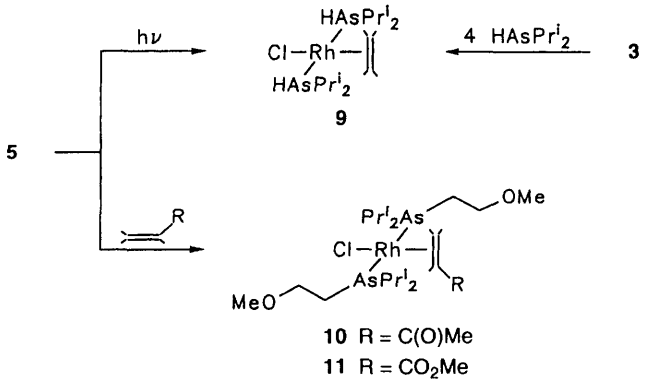
On treatment of compound **5** with CO, CNBu^t or H_2, the ethene is readily displaced and complexes **6**–**8** are formed in nearly quantitative yield. The carbonyl compound **6** shows a CO stretching frequency at 1974 cm^{-1} which is similar to that of *trans*-[RhCl(CO)(AsPr$^i_3$)$_2$].[10] In contrast to **6** and **7** which are yellow, moderately air-stable solids, the dihydride **8** is an orange-red air-sensitive oil. At 25 °C, the ^{1}H NMR spectrum displays only one signal for the hydride ligands at δ *ca.* −23, while at low temperatures two resonances (both doublets of doublets) at δ −13.4 and −22.2 are observed. We therefore assume that a rapid equilibrium between two enantiomeric octahedral (**A**, **C**) and one short-lived five-co-ordinate species (**B**) exists at room temperature [see equation (2)] which below −30 °C is frozen out giving a spectral pattern of a species containing two inequivalent arsinoether ligands. We note that for the related phosphinoether rhodium complex [RhH$_2$Cl(Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$] only one hydride resonance and one signal for each of the PCHCH_3 and OCH_3 protons is observed even at −80 °C.[2a] Furthermore, it is worth mentioning that in the reaction of **5** with H_2 ethane is formed and that on treatment of **8** with C_2H_4 the olefin complex **5** is regenerated.

During attempts to transform compound **5** to the isomeric hydrido(vinyl)rhodium(III) species [RhH(CH=CH$_2$)Cl(Pr$^i_2$AsCH$_2$CH$_2$OMe)$_2$], an unexpected observation has been made. Instead of an intramolecular C–H activation of the olefinic ligand, as occurs on irradiation of *trans*-[IrCl(C$_2$H$_4$)(Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$],[3a] the photolysis of **5** in benzene solution leads to the elimination of methyl vinyl ether and the formation of the bis(diisopropylarsine)rhodium(I) complex **9** (see Scheme 2). Since it has been proved by an independent experiment that under the same conditions the free arsinoether **I** does not react to give HAsPr$^i_2$ and CH$_2$=CHOMe, there is no doubt that the fragmentation of **5** is a rhodium-assisted process. Compound **9**, which is more conveniently prepared from **3** and four equivalents of HAsPr$^i_2$, is an orange-yellow crystalline solid that has been fully characterized by elemental analysis and spectroscopic means.

The ethene ligand in **5** cannot only be displaced by CO, CNBu^t and H_2 but also by substituted olefins (Scheme 2). The use of methyl vinyl ketone and methyl acrylate as olefinic substrates was initiated by our recent finding[11,12] that both



A **B** **C** (2)



Scheme 2

[{RhCl(PPr$^i_3$)$_2$}$_n$] and [IrCl(C$_8$H$_{14}$)(PPr$^i_3$)$_2$] react with CH$_2$=CHR [R = C(O)Me or CO$_2$Me] to give *via* π-co-ordination and subsequent C–H activation the octahedral rhodium(III) and iridium(III) derivatives [MH{CH=CHC(R)=O}Cl(PPr$^i_3$)$_2$] (M = Rh or Ir). However, the arsinoether complexes **10** and **11**, which are prepared from **5** and CH$_2$=CHR in pentane at room temperature, are thermally as well as photochemically quite inert. Even after prolonged heating of **10** or **11** in benzene solution to 70 °C no further rearrangement occurs. As in the ^{1}H and ^{13}C NMR spectra of complex **11** at room temperature two signals for the AsCHC*H*$_3$ protons and the AsCH*C*H$_3$ carbon atoms are observed, we conclude that the rotation about the rhodium–olefin bond is significantly hindered, likewise in some of the analogous alkyne rhodium compounds *trans*-[RhCl(RC≡CR′)(Pr$^i_2$AsCH$_2$CH$_2$OMe)$_2$] (R = Me or SiMe$_3$; R′ = Ph).

Alkyne, Allene, Vinylidene and Allenylidene Rhodium Complexes prepared from Alkynes.—Due to the lability of the Rh–C$_2$H$_4$ bond in complex **5**, the synthesis of the alkyne complexes **12**–**16** is straightforward and can be performed in pentane at −78 °C. Even under these conditions, the displacement of the olefin occurs readily and gives the products in virtually quantitative yield. Whereas **12**–**15** are yellow or orange microcrystalline solids, compound **16** is an oil at room temperature and somewhat more air-sensitive than the solid counterparts. For all the alkyne complexes correct elemental analyses have been obtained. The most characteristic feature in the ^{1}H NMR spectra of **12** and **13** is the doublet at δ 3.8–4.8 which is assigned to the ≡CH proton of the co-ordinated alkyne. The ^{13}C NMR spectra of **12**–**16** display two resonances at δ 60–90 (for **14** one is observed at δ 108) corresponding to the carbon atoms of the C≡C unit.

In contrast to the reaction of **5** with HC≡CPh and HC≡CCO$_2$Me a vinylidene instead of an alkyne rhodium complex is formed on treatment of the ethene compound with HC≡CMe or HC≡CBu^t. If the corresponding 1-alkyne (not in a large excess) is added at −78 °C to a pentane solution of **5** and the reaction mixture slowly warmed to room temperature, a characteristic change of colour from yellow to violet occurs and after stirring for 20 min (R = Me) or 3 h (R = Bu^t) the products **19** and **20** (Scheme 3) are generated in about 90% yield. Although attempts to isolate an intermediary species in these reactions have failed, we nevertheless believe that an alkyne rhodium compound *trans*-[RhCl(HC≡CR)(Pr$^i_2$AsCH$_2$CH$_2$OMe)$_2$] (R = Me or Bu^t) is initially formed. If the reaction mixture obtained from **5** and HC≡CBu^t is worked-up after 1 h (instead of 3 h), upon removal of the solvent an oily residue remains whose IR spectrum shows a band at 1833 cm^{-1} typical for a co-ordinated alkyne. In the IR spectra of the final product **20** an absorption at 1641 cm^{-1} is observed which corresponds to the C=C stretching frequency of the vinylidene ligand.

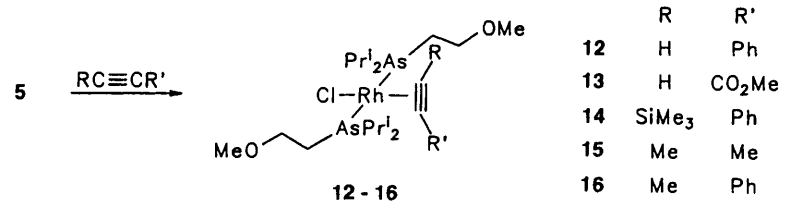
The analogous phenyl- and carboxymethyl-substituted vinylidene complexes **17** and **18** are prepared by UV irradiation of benzene solutions of **12** and **13** at room temperature. After 1 h the isomerization is complete. Whereas **17**, **18** and **20** are dark violet, rather low-melting solids, compound **19** is a violet oil which does not crystallize at room temperature. Diagnostic in the ^{1}H NMR spectra is a doublet at δ 0.3–1.8 for the vinylidene C=CHR proton, and in the ^{13}C NMR spectra a low-field signal at δ 282–293 which corresponds to the metal-bonded carbon atom of the Rh=C=CHR moiety.

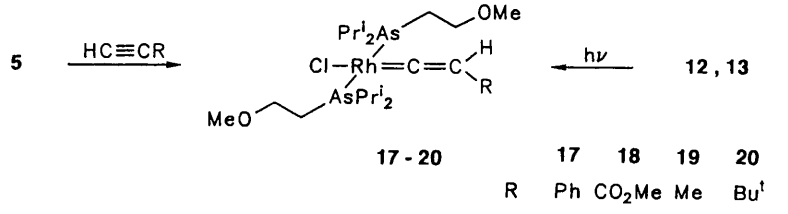
The reaction of **5** with HC≡CMe takes a different course if a large excess of the alkyne (**5**:HC≡CMe ≈ 1:90) is used. Under these conditions, instead of the methylvinylidene complex **19**, the isomeric allene rhodium compound **21** is obtained. The internal alkyne MeC≡CBu^t behaves similarly and upon treatment with **5** gives the *tert*-butylallene derivative **22** in excellent yield. The spectroscopic data of **22** strongly support the proposal (see Scheme 4) that it is the unsubstituted double bond of the allene which is co-ordinated to the metal. The ^{13}C NMR spectrum in particular is similar to those of the related bis(triisopropylphosphine) and bis(triisopropylarsine) rhodium complexes *trans*-[RhCl{CH$_2$=C=CH(CO$_2$Et)}(PPr$^i_3$)$_2$][13] and *trans*-[RhCl(CH$_2$=C=CHBu^t)(AsPr$^i_3$)$_2$],[10] the first of which has been structurally characterized by X-ray crystallography. Concerning the mechanism of the reaction of **5** with CH$_3$C≡CR (R = H or Bu^t), we assume that in the primary step the expected (but very labile) alkyne complex *trans*-[RhCl(CH$_3$C≡CR)(Pr$^i_2$AsCH$_2$CH$_2$OMe)$_2$] is formed which rearranges *via* a short-lived RhH(η^3-CH$_2$C$_2$CH$_3$) intermediate to the final product. There is some precedent for the metal-initiated transformation of an alkyne to the isomeric allene insofar as Richards and co-workers[14] as well as the authors[15] have described the formation of substituted allene rhenium and iridium complexes from reactive metal precursors and CH$_3$C≡CPh or CH$_3$C≡CCH$_3$, respectively.

The ^{1}H NMR spectrum of compound **21** deserves some comments. It shows three signals for the allene protons, one at relatively high field at δ 2.3 (in C$_6$D$_6$) for the equivalent protons of the metal-bound CH$_2$ group and two at lower field at δ 5.25 and 5.41 for the non-equivalent hydrogens (H$_{exo}$ and H$_{endo}$) of the unco-ordinated CH$_2$ allene unit. This assignment, which is consistent with data for analogous systems,[16] together with the appearance of four doublets for the diastereotopic CH$_3$ protons of the isopropyl groups, indicates a hindered rotation around the allene-to-rhodium bond and an effectively rigid structure of the whole molecule. Evidence for the non-fluxional behaviour on the NMR time-scale of the C$_3$H$_4$ ligand in **21** is equally provided by the ^{13}C NMR spectrum which reveals a large difference in the chemical shift between the signals of the two CH$_2$ carbons (δ 95.51 and 6.63).

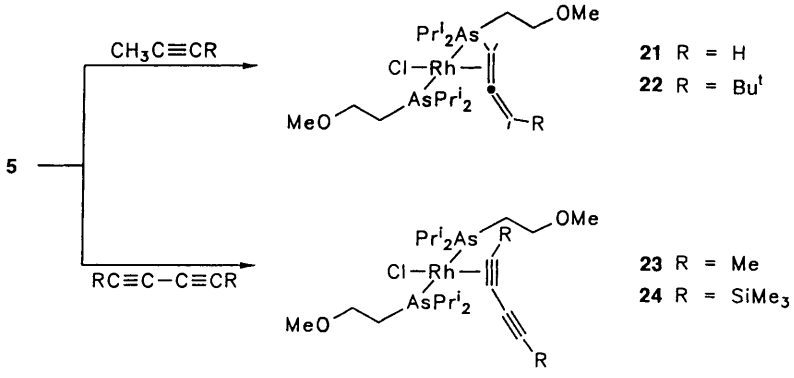
The buta-1,3-diyne derivatives MeC≡C–C≡CMe and Me$_3$SiC≡C–C≡CSiMe$_3$ react with compound **5** in pentane at low temperature to give instead of the expected dinuclear species the mononuclear complexes **23** and **24** in virtually quantitative yield. We assume that it is the steric bulk of the arsinoether ligands which prevents the co-ordination of *two* RhCl(Pr$^i_2$AsCH$_2$CH$_2$OMe)$_2$ units to the diyne molecule. The two compounds **23** (an orange-yellow low-melting solid) and **24** (an orange oil) are soluble in all common organic solvents, including pentane and hexane, and are only slightly air-sensitive. The structural proposal shown in Scheme 4 is particularly supported by the IR spectra in which a band at 2197 (**23**) or 2120 cm^{-1} (**24**) assigned to ν(C≡C) of a free alkyne moiety is observed apart from an absorption at 1904 (**23**) or 1828 cm^{-1} (**24**) for a co-ordinated alkyne.[17] In accordance with this, there are also two signals in the ^{1}H NMR spectrum of **23** for the two different methyl groups and in that of **24** for the two different trimethylsilyl groups. Equally, there are four signals in the ^{13}C NMR spectra due to the carbon atoms of the co-ordinated and unco-ordinated triple bond.

The synthesis of the allenylidene rhodium complexes **29**–**32** has been achieved as outlined in Scheme 5. In the first

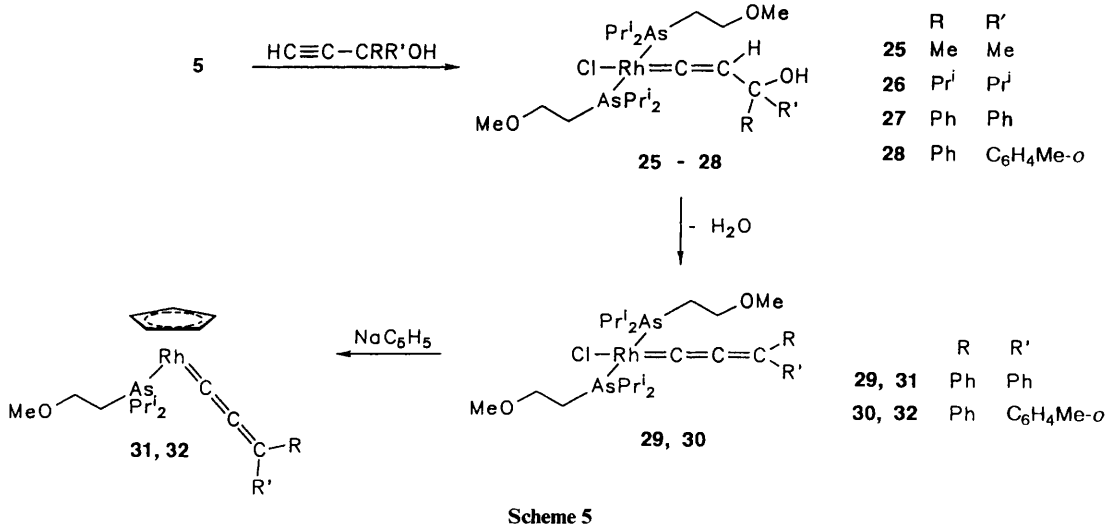




Scheme 3



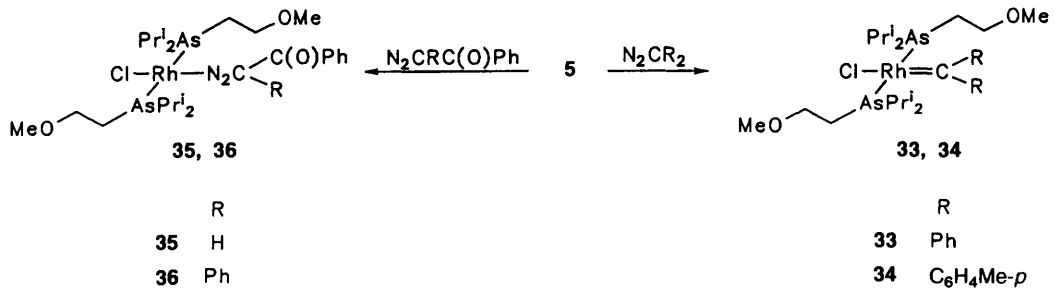
Scheme 4



Scheme 5

step, treatment of the ethene derivative **5** with the alkynol HC≡C–CRR'OH leads, for R = R' = alkyl at room temperature and for R = R' = aryl even at −78 °C, to the formation of the vinylidenes **25**–**28** which after column chromatography have been isolated as violet low-melting crystalline solids. The assumption that these compounds are formed *via* the isomeric alkyne complexes *trans*-[RhCl(HC≡CCRR'OH)(Pr$^i_2$AsCH$_2$CH$_2$OMe)$_2$] could not be substantiated by isolating an intermediate although a rapid colour change from orange to yellow after the addition of 1,1-diphenylprop-2-yne-1-ol to a pentane solution of **5** at −78 °C may be due to the formation of such a species. As far as the spectroscopic data of **25**–**28** are concerned, the most typical features are, as for the related compounds **17**–**20**, the low-field signals in the ^{13}C NMR spectra at δ 283–287 and 110–122, which are assigned to the C$^\alpha$ and C$^\beta$ vinylidene carbon atoms. In the IR spectra, a fairly broad band at 3400–3450 cm^{-1} is indicative of an OH group.

Whereas solutions of **25** and **26** in hexane or benzene rapidly decompose in the presence of Al_2O_3 or acidic substrates, compounds **27** and **28** react with alumina by abstraction of water to give the allenylidene rhodium(I) derivatives **29** and **30** in 80–90% yield. The red solids which have been characterized by elemental analysis are moderately air-sensitive and readily soluble in most organic solvents. They can be transformed to the cyclopentadienyl complexes **31** and **32** upon treatment with NaC_5H_5 in tetrahydrofuran (thf). After chromatographic



35, 36

	R
35	H
36	Ph

33, 34

	R
33	Ph
34	C_6H_4Me-*p*

Scheme 6

work-up, the allenylidene half-sandwiches are isolated as turquoise-blue oily substances. We note that the spectroscopic data of **29** and **30** are distinctly different from those of the corresponding rhodium vinylidenes **17–20** and **25–28** and in some respects resemble those of organic allenes.[18] Most diagnostic are the strong C=C=C stretchings in the IR spectra at *ca.* 1875 cm^{-1} (for **29**, **30**) and *ca.* 1910 cm^{-1} (for **31**, **32**) and the three low-field resonances in the ^{13}C NMR spectra at δ 160–250. In this context it should be mentioned that in the spectra of the square-planar rhodium allenylidenes **29** and **30** the signal of C^{α} of the Rh=C=C=C chain appears at somewhat higher field than that of C^{β}, while for **31** and **32** this situation is reversed.

Carbene and Diazoalkane Rhodium Derivatives prepared from Diazoalkane Precursors.—In contrast to the bis(triisopropylarsine) complex *trans*-[RhCl(C_2H_4)($AsPr^i_3$)$_2$] which upon treatment with N_2CPh_2 yields *trans*-[RhCl(N_2CPh_2)($AsPr^i_3$)$_2$],[19] the arsinoether derivative **5** reacts with diphenyldiazomethane in pentane under slightly reduced pressure (*ca.* 50 Torr) to give initially a brown-green oily product which in benzene solution after prolonged stirring (5 h) or short photolysis (20 min) affords the diphenylcarbene rhodium(I) compound *trans*-[RhCl(=CPh_2)($Pr^i_2AsCH_2CH_2OMe$)$_2$] **33** in moderate yield (Scheme 6). The *p*-tolyl derivative $N_2C(C_6H_4Me$-*p*$)_2$ behaves similarly and gives *trans*-[RhCl{=$C(C_6H_4Me$-*p*$)_2$}($Pr^i_2AsCH_2CH_2OMe$)$_2$] **34**. The brown-green intermediate which is also formed in this case seems to be a 1 : 1 adduct between [RhCl($Pr^i_2AsCH_2CH_2OMe$)$_2$] and N_2CR_2 in which the diaryldiazomethane moiety is possibly bonded *via* N *and* C to the metal. If an 'end-on' co-ordination mode as in *trans*-[RhCl(N_2CPh_2)(PPr^i_3)$_2$][20] were present, an absorption in the IR spectrum at 1900–2000 cm^{-1} would be expected which is, however, absent. Instead, a band of medium intensity at about 1670 cm^{-1} is observed. Since the ^1H NMR spectrum of the intermediate reveals that the arsinoether ligands are not equivalent, we assume that one of them is monodentate and one bidentate and that the rhodium centre is co-ordinated in an octahedral fashion. There is some precedent for such a bonding mode of a diazoalkane ligand. Stone and co-workers[21] have previously described the synthesis of the complexes [IrCl{$N_2C(CF_3)_2$}(PPh_3)$_2$] and *cis*-[Pt{$N_2C(CF_3)_2$}(PPh_3)$_2$] in which according to the spectroscopic data a *C,N*-chelated $N_2C(CF_3)_2$ unit is present.

The rhodium carbenes **33** and **34** which are low-melting air-sensitive materials have been characterized by elemental analysis and NMR spectroscopy. The most characteristic feature is the low-field signal for the carbene carbon atom in the ^{13}C NMR spectrum which displays a large Rh–C coupling of 32–33 Hz. It should be mentioned that in the reaction of **5** with diphenyldiazomethane small amounts of the trisubstituted ethene derivative Ph_2C=$CHCH_3$ are also formed. This is obtained on a catalytic route from C_2H_4 and N_2CPh_2 by using compound **3** as catalyst.[20,22]

The diazocarbonyl derivatives $N_2CHC(O)Ph$ and $N_2CPhC(O)Ph$ react with **5** to give complexes **35** and **36** in which the intact N_2CRR' moiety is probably bonded 'end-on' through the nitrogen atom to the metal centre. Diagnostic for this type of co-ordination is a N–N stretching frequency in the IR at 1920–1930 cm^{-1} and a signal in the ^{13}C NMR spectrum for the N_2C carbon atom at δ 83.06 (**35**) or 101.09 (**36**). Despite the fact that both compounds are thermally not very stable (decomposition temperature about 30 °C), all attempts to transform them to the corresponding rhodium carbenes *trans*-[RhCl{=CR(COPh)}($Pr^i_2AsCH_2CH_2OMe$)$_2$] have remained unsuccessful.

Experimental

All reactions were carried out under an atmosphere of argon by Schlenk-tube techniques. The starting materials $HAsPr^i_2$,[9] [{RhCl(C_8H_{14})$_2$}$_2$] **1**[23] and [{RhCl(C_2H_4)$_2$}$_2$] **3**[24] were prepared by published methods. The alkenes and alkynes were commercial products from Aldrich and ABCR. The NMR spectra were recorded on Bruker AC 200 and Bruker AMX 400 spectrometers (s = singlet, d = doublet, t = triplet, q = quartet, spt = septet, m = multiplet, br = broadened signal), the IR spectra on a Perkin-Elmer 1420 spectrometer and the mass spectra on Varian CH7 MAT and Finnigan 90 MAT instruments. Melting and decomposition points were determined by differential thermal analysis.

Preparations.—$Pr^i_2AsCH_2CH_2OMe$ **I**. In a three-necked flask (250 cm^3) a solution of $HAsPr^i_2$ (5.20 g, 32.0 mmol) in thf (60 cm^3) was treated at 0 °C dropwise with a 1.14 mol dm^{-3} solution of LiBu (32.0 cm^3) in hexane. After warming to room temperature, the solution was stirred for 30 min and then heated under reflux for 1 h. At reflux temperature, a solution of $ClCH_2CH_2OMe$ (3.30 g, 35.0 mmol) in thf (5 cm^3) was added dropwise to the reaction mixture which slowly led to the formation of a white microcrystalline precipitate. After 30 min under reflux, the solution was cooled to room temperature and then 100 cm^3 of a saturated aqueous solution of NH_4Cl were added. The ether phase was separated, the aqueous solution was extracted three times with diethyl ether (50 cm^3 each), and the combined ethereal phases were dried over Na_2SO_4 for 5 h. The sodium salt was filtered off, the ether was removed and the oily residue was distilled under reduced pressure (*ca.* 2 Torr). At 50–51 °C, a colourless air-sensitive liquid was obtained (D = 1.047 g cm^{-3}) which for analytical characterization was converted with MeI to the arsonium salt [$MeAs(Pr^i)_2CH_2CH_2OMe$]I (Found: C, 33.35; H, 6.85. Calc. for $C_{10}H_{24}AsIO$: C, 33.15; H, 6.70%). NMR: ^1H (400 MHz, C_6D_6), δ 3.48 (m, 2 H, CH_2OCH_3), 3.13 (s, 3 H, CH_2OCH_3), 1.65 (m, 2 H, $AsCH_2$), 1.63 [spt, J(HH) 7.2, 2 H, $AsCHCH_3$], 1.08 and 1.05 [both d, J(HH) 7.2 Hz, 12 H, $AsCHCH_3$]; ^{13}C (100.6 MHz, C_6D_6), δ 72.32 (s, CH_2OCH_3), 58.04 (s, CH_2OCH_3), 23.60 (s, $AsCHCH_3$), 21.95 (s, $AsCH_2$), 20.93 and 20.04 (both s, $AsCHCH_3$).

[{RhCl(C_8H_{14})($Pr^i_2AsCH_2CH_2OMe$)}$_2$] **2**. A suspension of compound **1** (60 mg, 0.08 mmol) in pentane (10 cm^3) was treated with **I** (35 μl, 0.16 mmol) and stirred for 30 min at room temperature. The solution was brought to dryness *in vacuo*, the

oily residue was dissolved in benzene (0.3 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With benzene–hexane (1 : 1), an orange-yellow fraction was eluted from which the solvent was removed *in vacuo*. The oily residue was recrystallized from thf–pentane (1 : 10) to give, after cooling to −78 °C, orange-yellow crystals: yield 61 mg (81%), m.p. 35 °C (decomp.) (Found: C, 43.20; H, 7.55. Calc. for $C_{34}H_{70}As_2Cl_2O_2Rh_2$: C, 43.55; H, 7.55%). NMR: ^1H (200 MHz, C_6D_6), δ 3.71–3.18, 2.70–2.35 and 1.59–1.40 (all m, 28 H, C_8H_{14}), 3.66 (m, 4 H, CH_2OCH_3), 3.14 (s, 6 H, CH_2OCH_3), 1.99 [spt, *J*(HH) 7.2, 4 H, $AsCHCH_3$], 1.63 (m, 4 H, $AsCH_2$), 1.33 and 1.13 [both d, *J*(HH) 7.2 Hz, 24 H, $AsCHCH_3$].

$[\{RhCl(C_2H_4)(Pr^i_2AsCH_2CH_2OMe)\}_2]$ **4**. A solution of compound **3** (50 mg, 0.13 mmol) in diethyl ether (2 cm^3) was treated dropwise with a solution of **I** (54 μl, 0.26 mmol) in diethyl ether (3 cm^3) and stirred for 1 h at room temperature. The solvent was removed, the oily residue was thoroughly dried *in vacuo* (10^{-3} Torr) and then recrystallized from pentane (10 cm^3) at −78 °C. Orange needles were obtained which were repeatedly washed with small amounts of pentane (0 °C) and dried: yield 83 mg (83%), m.p. 45 °C (decomp.) (Found: C, 34.05; H, 6.85. Calc. for $C_{22}H_{50}As_2Cl_2O_2Rh_2$: C, 34.15; H, 6.50%). NMR: ^1H (200 MHz, C_6D_6), δ 3.58 (m, 4 H, CH_2OCH_3), 3.15 (br s, 8 H, C_2H_4), 3.09 (s, 6 H, CH_2OCH_3), 1.88 [spt, *J*(HH) 7.1, 4 H, $AsCHCH_3$], 1.58 (m, 4 H, $AsCH_2$), 1.25 and 1.05 [both d, *J*(HH) 7.1 Hz, 24 H, $AsCHCH_3$].

trans-$[RhCl(C_2H_4)(Pr^i_2AsCH_2CH_2OMe)_2]$ **5**. A solution of compound **3** (50 mg, 0.13 mmol) in diethyl ether (10 cm^3) was treated with **I** (108 μl, 0.52 mmol) and stirred for 1 h at room temperature. A change of colour from orange to orange-red was observed. The solvent was removed *in vacuo*, the oily residue was dissolved in hexane (1 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, an orange-yellow fraction was eluted which was brought to dryness *in vacuo*. The residue was recrystallized from pentane to give, after cooling to −78 °C, orange-yellow crystals: yield 123 mg (78%), m.p. 41 °C (decomp.) (Found: C, 39.45; H, 7.85. Calc. for $C_{20}H_{46}As_2ClO_2Rh$: C, 39.60; H, 7.65%). NMR: ^1H (200 MHz, C_6D_6), δ 3.69 (m, 4 H, CH_2OCH_3), 3.15 (s, 6 H, CH_2OCH_3), 2.81 [d, *J*(RhH) 2.2, 4 H, C_2H_4], 2.29 [spt, *J*(HH) 7.2, 4 H, $AsCHCH_3$], 1.82 (m, 4 H, $AsCH_2$), 1.34 and 1.19 [both d, *J*(HH) 7.2 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 70.19 (s, CH_2OCH_3), 58.09 (s, CH_2OCH_3), 34.76 [d, *J*(RhC) 14.6 Hz, C_2H_4], 24.34 (s, $AsCHCH_3$), 20.70 and 20.20 (both s, $AsCHCH_3$), 17.30 (s, $AsCH_2$).

trans-$[RhCl(CO)(Pr^i_2AsCH_2CH_2OMe)_2]$ **6**. Carbon monoxide was passed through a solution of **5** (61 mg, 0.10 mmol) in pentane (10 cm^3) at room temperature for 10 s. After the solution was stirred for 15 min, it was concentrated *in vacuo* until the first crystals precipitated. Further cooling to −78 °C led to the formation of a pale yellow microcrystalline solid which was separated, repeatedly washed with pentane (0 °C) and dried: yield 60 mg (98%), m.p. 50 °C (decomp.) (Found: C, 38.10; H, 7.20. Calc. for $C_{19}H_{42}As_2ClO_3Rh$: C, 37.60; H, 7.00%). IR (KBr), ν(CO) 1974 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 3.77 (m, 4 H, CH_2OCH_3), 3.34 (s, 6 H, CH_2OCH_3), 2.49 [spt, *J*(HH) 7.2, 4 H, $AsCHCH_3$], 2.19 (m, 4 H, $AsCH_2$), 1.33 and 1.32 [both d, *J*(HH) 7.2 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 188.51 [d, *J*(RhC) 71.5 Hz, CO], 70.24 (s, CH_2OCH_3), 58.04 (s, CH_2OCH_3), 26.14 (s, $AsCHCH_3$), 21.29 (s, $AsCH_2$), 20.25 and 19.81 (both s, $AsCHCH_3$).

trans-$[RhCl(CNBu^t)(Pr^i_2AsCH_2CH_2OMe)_2]$ **7**. A solution of **5** (53 mg, 0.09 mmol) in pentane (8 cm^3) was treated at −78 °C with *tert*-butyl isocyanide (10 μl, 0.09 mmol) and, after warming to room temperature, stirred for 15 min. A gradual brightening of the yellow solution was observed. The solvent was removed *in vacuo*, and the oily residue was recrystallized from pentane to give, after cooling to −78 °C, yellow air-sensitive crystals: yield 53 mg (89%), m.p. 38 °C (decomp.) (Found: C, 41.65; H, 7.95; N, 2.00. Calc. for $C_{23}H_{51}As_2ClNO_2Rh$: C, 41.75; H, 7.75; N, 2.10%). IR (C_6H_6), ν(C≡N) 2141 and 2104 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 3.92 (m, 4 H, CH_2OCH_3), 3.18 (s, 6 H, CH_2OCH_3), 2.32 [spt, *J*(HH) 7.1, 4 H, $AsCHCH_3$], 2.25 (m, 4 H, $AsCH_2$), 1.44 and 1.28 [both d, *J*(HH) 7.1 Hz, 24 H, $AsCHCH_3$], 1.11 [s, 9 H, $C(CH_3)_3$].

$[RhH_2Cl(Pr^i_2AsCH_2CH_2OMe)_2]$ **8**. Hydrogen was passed through a solution of **5** (57 mg, 0.09 mmol) in pentane (7 cm^3) at room temperature for 30 s. A change of colour from orange-yellow to red was observed. After the solution was stirred for 5 min, the solvent was removed *in vacuo*, the oily residue was dissolved in hexane (3 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With diethyl ether–hexane (2 : 1), an orange-red fraction was eluted which was brought to dryness *in vacuo*. The remaining orange-red oil was thoroughly dried *in vacuo* (10^{-3} Torr): yield 54 mg (99%) (Found: C, 37.30; H, 7.40. Calc. for $C_{18}H_{44}As_2ClO_2Rh$: C, 37.20; H, 7.65%). IR (C_6H_6), ν(RhH) 2079 cm^{-1}. NMR: ^1H (200 MHz, $C_6D_5CD_3$), δ 3.73 (m, 4 H, CH_2OCH_3), 3.17 (s, 6 H, CH_2OCH_3), 2.12 [spt, *J*(HH) 6.9, 4 H, $AsCHCH_3$], 1.87 (m, 4 H, $AsCH_2$), 1.27 and 1.25 [both d, *J*(HH) 6.9, 24 H, $AsCHCH_3$], −23.06 [d, *J*(RhH) 19.7 Hz, 2 H, RhH_2].

trans-$[RhCl(C_2H_4)(HAsPr^i_2)_2]$ **9**. A solution of **5** (37.mg, 0.06 mmol) in $[^2H_6]$benzene (0.5 cm^3) was irradiated at room temperature in an NMR tube for 10 h. A gradual change of colour from orange-yellow to red was observed. The solution was transferred into a Schlenk tube and slowly condensed into another cooled (−78 °C) Schlenk tube. The clear condensate was identified as methyl vinyl ether by ^1H and ^{13}C NMR data.[25] The orange oily residue in the first Schlenk tube was dried *in vacuo* (10^{-3} Torr) and spectroscopically identified as **9**. An independent synthesis of **9** is as follows. A solution of **3** (39 mg, 0.10 mmol) in diethyl ether (5 cm^3) was treated with four equivalents of $HAsPr^i_2$ (67 μl, 0.40 mmol). After stirring for 20 min at room temperature, the solvent was removed and from the residue, after recrystallization from pentane (−78 °C), an orange-yellow microcrystalline solid was obtained: yield 38 mg (78%), m.p. 118 °C (decomp.) (Found: C, 34.40; H, 7.10. Calc. for $C_{14}H_{34}As_2ClRh$: C, 34.25; H, 7.00%). NMR: ^1H (200 MHz, C_6D_6), δ 2.96 [d, *J*(RhH) 2.4, 4 H, C_2H_4], 2.53 (m, 2 H, AsH), 2.12 [spt, *J*(HH) 7.1, 4 H, $AsCHCH_3$], 1.21 and 1.13 [both d, *J*(HH) 7.1 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 31.93 [d, *J*(RhC) 13.9 Hz, C_2H_4], 25.30 (s, $AsCHCH_3$), 22.60 and 21.54 (s, $AsCHCH_3$).

trans-$[RhCl\{H_2C{=}CHC(O)Me\}(Pr^i_2AsCH_2CH_2OMe)_2]$ **10**. A solution of **5** (61 mg, 0.10 mmol) in pentane (10 cm^3) was treated with methyl vinyl ketone (8 μl, 0.10 mmol) and stirred for 45 min at room temperature. A gradual change of colour from orange to orange-red was observed. The solvent was removed *in vacuo*, and the residue was recrystallized from pentane (5 cm^3) to give, after cooling to −78 °C, orange-red crystals: yield 63 mg (98%), m.p. 36 °C (Found: C, 40.45; H, 7.50. Calc. for $C_{22}H_{48}As_2ClO_3Rh$: C, 40.75; H, 7.45%). IR (KBr), ν(C=O) 1673 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 3.89 [br dd, $^3J(HH_{trans})$ 10.7, $^3J(HH_{cis})$ 7.1, 1 H, $H_2C{=}CH$], 3.78 (m, 4 H, CH_2OCH_3), 3.09 (s, 6 H, CH_2OCH_3), 3.07 [br d, $^3J(HH_{trans})$ 10.7, 1 H, $H_2C{=}CH$], 2.59 [br d, $^3J(HH_{cis})$ 7.1, 1 H, $H_2C{=}CH$], 2.39 [spt, *J*(HH) 6.8, 4 H, $AsCHCH_3$], 2.30 [s, 3 H, $C(O)CH_3$], 1.64 (m, 4 H, $AsCH_2$), 1.34 and 1.18 [both d, *J*(HH) 6.8 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 204.76 [d, *J*(RhC) 1.8, $C(O)CH_3$], 70.15 (s, CH_2OCH_3), 58.07 (s, CH_2OCH_3), 48.17 [d, *J*(RhC) 14.5, $H_2C{=}CH$], 31.05 [s, $C(O)CH_3$], 28.57 [d, *J*(RhC) 14.0 Hz, $H_2C{=}CH$], 25.14 (s, $AsCHCH_3$), 21.15 and 20.17 (both s, $AsCHCH_3$), 18.12 (s, $AsCH_2$).

trans-$[RhCl\{H_2C{=}CHCO_2Me\}(Pr^i_2AsCH_2CH_2OMe)_2]$ **11**. This compound was prepared as described for **10**, using **5** (73 mg, 0.12 mmol) and methyl acrylate (11 μl, 0.12 mmol) as starting materials. An orange-red microcrystalline solid was obtained: yield 75 mg (94%), m.p. 39 °C (Found: C, 39.90; H, 7.50. Calc. for $C_{22}H_{48}As_2ClO_4Rh$: C, 39.75; H, 7.30%). IR

(KBr), ν(C=O) 1706 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 3.76 [br dd, $^3J(HH_{trans})$ 10.3, $^3J(HH_{cis})$ 7.0, 1 H, $H_2C{=}CH$], 3.72 (m, 4 H, CH_2OCH_3), 3.44 (s, 3 H, CO_2CH_3), 3.19 (s, 6 H, CH_2OCH_3), 3.16 [br dd, $^3J(HH_{trans})$ 10.3, $^2J(HH)$ 1.1, 1 H, $H_2C{=}CH$], 2.74 [br dd, $^3J(HH_{cis})$ 7.1, $^2J(HH)$ 1.1, 1 H, $H_2C{=}CH$], 2.46 [spt, $J(HH)$ 7.2, 4 H, $AsCHCH_3$], 2.03 (m, 4 H, $AsCH_2$), 1.39, 1.33, 1.22 and 1.17 [all d, $J(HH)$ 7.2 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 176.43 [d, $J(RhC)$ 2.5, CO_2CH_3], 70.29 (s, CH_2OCH_3), 58.06 (s, CH_2OCH_3), 51.04 (s, CO_2CH_3), 38.57 [d, $J(RhC)$ 15.3, $H_2C{=}CH$], 31.43 [d, $J(RhC)$ 14.3 Hz, $H_2C{=}CH$], 25.25 (s, $AsCHCH_3$), 21.19 and 20.91 (both s, $AsCHCH_3$), 18.41 (s, $AsCH_2$).

trans-[RhCl(HC≡CPh)($Pr^i_2AsCH_2CH_2OMe$)$_2$] **12**. A solution of compound **5** (76 mg, 0.13 mmol) in pentane (7 cm^3) was treated at −78 °C with phenylacetylene (14 μl, 0.13 mmol) and stirred for 30 s at −78 °C. A spontaneous change of colour from orange-yellow to yellow was observed. The solvent was removed *in vacuo*, the residue was washed twice with small amounts of pentane and recrystallized from pentane (3 cm^3) to give, after cooling to −78 °C, an orange-yellow microcrystalline solid: yield 74 mg (86%), m.p. 54 °C (decomp.) (Found: C, 45.95; H, 7.55. Calc. for $C_{26}H_{48}As_2ClO_2Rh$: C, 45.85; H, 7.10%). IR (KBr), ν(C≡C) 1810 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 8.20 [dd, $^3J(HH)$ 7.5, $^4J(HH)$ 1.1, 2 H, *o*-H of C_6H_5], 7.18–6.99 (m, 3 H, *m*-H and *p*-H of C_6H_5), 3.86 [d, $J(RhH)$ 2.4, 1 H, $HC{\equiv}C$], 3.60 (m, 4 H, CH_2OCH_3), 3.08 (s, 6 H, CH_2OCH_3), 2.34 [spt, $J(HH)$ 7.1, 2 H, $AsCHCH_3$], 2.01 [spt, $J(HH)$ 7.3, 2 H, $AsCHCH_3$], 1.77 (m, 4 H, $AsCH_2$), 1.36 and 1.21 [both d, $J(HH)$ 7.1, 12 H, $AsCHCH_3$], 1.33 and 1.09 [both d, $J(HH)$ 7.3 Hz, 12 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 130.89 (s, C^1 of C_6H_5), 128.97, 128.26 and 127.14 (all s, C^{2-6} of C_6H_5), 75.32 [d, $J(RhC)$ 15.7, $HC{\equiv}C$], 69.81 (s, CH_2OCH_3), 69.23 [d, $J(RhC)$ 13.9 Hz, $HC{\equiv}C$], 57.79 (s, CH_2OCH_3), 25.00 and 23.52 (both s, $AsCHCH_3$), 20.74, 20.45, 20.34 and 19.44 (all s, $AsCHCH_3$), 18.28 (s, $AsCH_2$).

trans-[RhCl(HC≡CCO_2Me)($Pr^i_2AsCH_2CH_2OMe$)$_2$] **13**. This compound was prepared as described for **12**, using **5** (46 mg, 0.08 mmol) and methyl propiolate (7 μl, 0.08 mmol) as starting materials. Orange-yellow crystals were obtained: yield 50 mg (99%), m.p. 25 °C (decomp.) (Found: C, 40.25; H, 7.35. Calc. for $C_{22}H_{46}As_2ClO_4Rh$: C, 39.85; H, 7.00%). IR (KBr), ν(C≡C) 1792, ν(C=O) 1685 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 4.75 [d, $J(RhH)$ 2.4, 1 H, $HC{\equiv}C$], 3.74 (m, 4 H, CH_2OCH_3), 3.50 (s, 3 H, CO_2CH_3), 3.20 (s, 6 H, CH_2OCH_3), 2.22 [spt, $J(HH)$ 7.2, 4 H, $AsCHCH_3$], 1.91 (m, 4 H, $AsCH_2$), 1.32 [d, $J(HH)$ 7.3, 12 H, $AsCHCH_3$], 1.17 [d, $J(HH)$ 7.1 Hz, 12 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 157.26 (s, CO_2CH_3), 88.63 [d, $J(RhC)$ 14.8, $HC{\equiv}C$], 69.85 (s, CH_2OCH_3), 66.24 [d, $J(RhC)$ 16.6 Hz, $HC{\equiv}C$], 58.05 (s, CH_2OCH_3), 51.43 (s, CO_2CH_3), 24.47 (s, $AsCHCH_3$), 20.44 and 19.82 (both s, $AsCHCH_3$), 18.83 (s, $AsCH_2$).

trans-[RhCl($Me_3SiC{\equiv}CPh$)($Pr^i_2AsCH_2CH_2OMe$)$_2$] **14**. A solution of **5** (86 mg, 0.14 mmol) in pentane (8 cm^3) was treated at −78 °C with $Me_3SiC{\equiv}CPh$ (28 μl, 0.14 mmol) and stirred at −78 °C for 30 s. A change of colour from orange-yellow to yellow was observed. The solvent was removed *in vacuo*, the residue was washed twice with small amounts of pentane and recrystallized from pentane (2 cm^3) to give, after cooling to −78 °C, orange-yellow crystals: yield 109 mg (98%), m.p. 52 °C (decomp.) (Found: C, 46.45; H, 7.75. Calc. for $C_{29}H_{56}As_2ClO_2RhSi$: C, 46.25; H, 7.50%). IR (KBr), ν(C≡C) 1829 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 8.28 [dd, $^3J(HH)$ 6.8, $^4J(HH)$ 1.3, 2 H, *o*-H of C_6H_5], 7.19–7.00 (m, 3 H, *m*-H and *p*-H of C_6H_5), 3.54 (m, 4 H, CH_2OCH_3), 3.06 (s, 6 H, CH_2OCH_3), 2.28 and 2.23 [both spt, $J(HH)$ 7.2, 4 H, $AsCHCH_3$], 1.79 (m, 4 H, $AsCH_2$), 1.40, 1.38, 1.20 and 1.04 [all d, $J(HH)$ 7.2 Hz, 24 H, $AsCHCH_3$], 0.46 [s, 9 H, $Si(CH_3)_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 131.14 (s, C^1 of C_6H_5), 129.43, 128.80 and 128.09 (all s, C^{2-6} of C_6H_5), 107.98 [d, $J(RhC)$ 17.6, $C_6H_5C{\equiv}C$], 75.10 [d, $J(RhC)$ 13.9 Hz, $(CH_3)_3SiC{\equiv}C$], 69.85 (s, CH_2OCH_3), 57.85 (s, CH_2OCH_3), 25.26 [s, $Si(CH_3)_3$], 24.20 and 24.16 (both s, $AsCHCH_3$), 21.40, 21.25, 20.22 and 20.19 (all s, $AsCHCH_3$), 18.57 (s, $AsCH_2$).

trans-[RhCl(MeC≡CMe)($Pr^i_2AsCH_2CH_2OMe$)$_2$] **15**. A solution of **5** (97 mg, 0.16 mmol) in pentane (10 cm^3) was treated at −78 °C with but-2-yne (25 μl, 0.32 mmol) and, after warming to room temperature, stirred for 30 min. The solvent was removed *in vacuo*, the oily residue was dissolved in hexane (2 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, an orange-yellow fraction was eluted which was brought to dryness *in vacuo*. The oily residue was recrystallized from pentane (1 cm^3) to give, after cooling to −78 °C, orange-yellow crystals: yield 98 mg (96%), m.p. 31 °C (Found: C, 41.30; H, 7.90. Calc. for $C_{22}H_{48}As_2ClO_2Rh$: C, 41.75; H, 7.65%). IR (KBr), ν(C≡C) 1810 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 3.78 (m, 4 H, CH_2OCH_3), 3.21 (s, 6 H, CH_2OCH_3), 2.24 [spt, $J(HH)$ 7.2, 4 H, $AsCHCH_3$], 1.94 [d, $J(RhH)$ 0.7, 6 H, $CH_3C{\equiv}CCH_3$], 1.82 (m, 4 H, $AsCH_2$), 1.40 and 1.23 [both d, $J(HH)$ 7.2 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 70.27 (s, CH_2OCH_3), 59.13 [d, $J(RhC)$ 14.8 Hz, $CH_3C{\equiv}CCH_3$], 57.97 (s, CH_2OCH_3), 24.45 (s, $AsCHCH_3$), 20.85 and 20.28 (both s, $AsCHCH_3$), 18.48 (s, $AsCH_2$), 11.15 (s, $CH_3C{\equiv}CCH_3$).

trans-[RhCl(MeC≡CPh)($Pr^i_2AsCH_2CH_2OMe$)$_2$] **16**. This compound was prepared as described for **15**, using **5** (63 mg, 0.10 mmol) and 1-phenylprop-1-yne (13 μl, 0.10 mmol) as starting materials. An orange-yellow oil was obtained: yield 72 mg (98%) (Found: C, 46.80; H, 7.10. Calc. for $C_{27}H_{50}As_2ClO_2Rh$: C, 46.45; H, 7.25%). IR (KBr), ν(C≡C) 1892 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 8.04 [dd, $^3J(HH)$ 8.2, $^4J(HH)$ 1.3, 2 H, *o*-H of C_6H_5], 7.21–6.98 (m, 3 H, *m*-H and *p*-H of C_6H_5), 3.64 (m, 4 H, CH_2OCH_3), 3.09 (s, 6 H, CH_2OCH_3), 2.26 [spt, $J(HH)$ 7.3, 2 H, $AsCHCH_3$], 2.23 [d, $J(RhH)$ 1.1, 3 H, $H_3CC{\equiv}C$], 2.16 [spt, $J(HH)$ 7.1, 2 H, $AsCHCH_3$], 1.76 (m, 4 H, $AsCH_2$), 1.38 and 1.12 [both d, $J(HH)$ 7.1, 12 H, $AsCHCH_3$], 1.35 and 1.20 [both d, $J(HH)$ 7.3 Hz, 12 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 130.54 (s, C^1 of C_6H_5), 129.80, 128.24 and 126.03 (all s, C^{2-6} of C_6H_5), 78.29 [d, $J(RhC)$ 15.7, $C_6H_5C{\equiv}C$], 70.03 (s, CH_2OCH_3), 65.11 [d, $J(RhC)$ 14.8 Hz, $CH_3C{\equiv}C$], 57.81 (s, CH_2OCH_3), 25.15 and 24.43 (both s, $AsCHCH_3$), 20.98, 20.80, 20.44 and 20.02 (all s, $AsCHCH_3$), 19.05 (s, $AsCH_2$), 12.71 (s, $CH_3C{\equiv}C$).

trans-[RhCl(=C=CHPh)($Pr^i_2AsCH_2CH_2OMe$)$_2$] **17**. A solution of **12** (74 mg, 0.11 mmol) in benzene (0.5 cm^3) was irradiated at room temperature in an NMR tube for 1 h. A gradual change of colour from orange-yellow to deep violet was observed. The solvent was removed *in vacuo*, the oily residue was dissolved in hexane (1 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, a violet fraction was eluted which was brought to dryness *in vacuo*. The oily residue was recrystallized from pentane (2 cm^3) to give, after cooling to −78 °C, violet crystals: yield 72 mg (96%), m.p. 56 °C (decomp.) (Found: C, 45.90; H, 7.30. Calc. for $C_{26}H_{48}As_2ClO_2Rh$: C, 45.85; H, 7.10%). IR (KBr), ν(C=C), 1639 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 7.25–7.06 (m, 2 H, *o*-H of C_6H_5), 6.90–6.82 (m, 3 H, *m*-H and *p*-H of C_6H_5), 3.78 (m, 4 H, CH_2OCH_3), 3.09 (s, 6 H, CH_2OCH_3), 2.41 [spt, $J(HH)$ 7.1, 4 H, $AsCHCH_3$], 2.27 (m, 4 H, $AsCH_2$), 1.79 [d, $J(RhH)$ 1.5, 1 H, =C=CH], 1.33 and 1.22 [both d, $J(HH)$ 7.1 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 292.97 [d, $J(RhC)$ 53.4, =C=CH], 129.67 (s, C^1 of C_6H_5), 128.65, 128.25 and 125.27 (all s, C^{2-6} of C_6H_5), 114.76 [d, $J(RhC)$ 15.5, =C=CH], 70.15 (s, CH_2OCH_3), 57.92 (s, CH_2OCH_3), 25.47 [d, $J(RhC)$ 2.5, $AsCHCH_3$], 20.65 and 19.83 (both s, $AsCHCH_3$), 20.17 [d, $J(RhC)$ 2.5 Hz, $AsCH_2$].

trans-[RhCl(=C=$CHCO_2Me$)($Pr^i_2AsCH_2CH_2OMe$)$_2$] **18**. This compound was prepared as described for **17**, using **13** (50 mg, 0.08 mmol) as the starting material. Violet crystals were obtained: yield 47 mg (89%), m.p. 59 °C (decomp.) (Found: C, 39.70; H, 7.15. Calc. for $C_{22}H_{46}As_2ClO_4Rh$: C, 39.85; H, 7.00%). IR (KBr), ν(C=O) 1701, ν(C=C) 1635 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 3.75 (m, 4 H, CH_2OCH_3), 3.46 (s, 3 H,

CO_2CH_3), 3.21 (s, 6 H, CH_2OCH_3), 2.40 [spt, J(HH) 7.1, 4 H, AsC*H*CH_3], 2.27 (m, 4 H, $AsCH_2$), 1.60 [d, J(RhH) 1.3, 1 H, =C=CH], 1.29 and 1.19 [both d, J(HH) 7.1 Hz, 24 H, AsCHC*H*$_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 281.91 [d, J(RhC) 56.0, =*C*=CH], 158.42 (s, *C*O_2CH_3), 107.91 [d, J(RhC) 15.3 Hz, =C=*C*H], 69.91 (s, *C*H_2OCH_3), 58.01 (s, CH_2OCH_3), 50.53 (s, CO_2CH_3), 25.61 (s, As*C*HCH_3), 20.41 and 19.63 (both s, AsCH*C*H_3), 19.79 (s, $AsCH_2$).

trans-[RhCl(=C=CHMe)($Pr^i_2AsCH_2CH_2OMe)_2$] **19**. A solution of **5** (73 mg, 0.12 mmol) in pentane (10 cm^3) was treated at −78 °C with propyne (*ca.* 20 mg, 0.48 mmol) and, after warming to room temperature, stirred for 20 min. A change of colour from orange-yellow to violet-brown was observed. The solvent was removed *in vacuo*, the residue was dissolved in benzene (0.5 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane–benzene (1:1), a violet fraction was eluted which was brought to dryness *in vacuo*. The remaining violet oil was dried thoroughly *in vacuo* (10^{-3} Torr): yield 65 mg (87%) (Found: C, 40.95; H, 7.60. Calc. for $C_{21}H_{46}As_2ClO_2Rh$: C, 40.75; H, 7.50%). IR (C_6H_6), ν(C=C) 1681 cm^{-1}. NMR: ^{1}H (200 MHz, C_6D_6), δ 3.80 (m, 4 H, C*H*$_2$OCH$_3$), 3.15 (s, 6 H, CH_2OCH_3), 2.38 [spt, J(HH) 7.3, 4 H, AsC*H*CH_3], 1.90 (m, 4 H, $AsCH_2$), 1.81 [d, J(RhH) 7.5, 3 H, =C=CHC*H*$_3$], 1.33 and 1.24 [both d, J(HH) 7.3, 24 H, AsCHC*H*$_3$], 0.60 [dq, J(HH) 7.5, J(RhH) 1.5 Hz, 1 H, =C=CH]; ^{13}C (50.3 MHz, C_6D_6), δ 287.54 [d, J(RhC) 53.7, =*C*=CH], 101.73 [d, J(RhC) 14.7 Hz, =C=*C*H], 70.24 (s, *C*H_2OCH_3), 57.94 (s, CH_2OCH_3), 24.86 (s, As*C*HCH_3), 20.54 and 19.62 (both s, AsCH*C*H_3), 17.19 (s, $AsCH_2$), 1.35 (s, =C=CH*C*H_3).

trans-[RhCl(=C=CHBu^t)($Pr^i_2AsCH_2CH_2OMe)_2$] **20**. This compound was prepared as described for **19**, using **5** (37 mg, 0.06 mmol) and 3,3-dimethylbut-1-yne (15 μl, 0.12 mmol) as starting materials. Violet crystals were obtained: yield 36 mg (91%), m.p. 29 °C (decomp.) (Found: C, 43.65; H, 8.15. Calc. for $C_{24}H_{52}As_2ClO_2Rh$: C, 43.60; H, 7.95%). IR (C_6H_6), ν(C=C) 1641 cm^{-1}. NMR: ^{1}H (200 MHz, C_6D_6), δ 3.81 (m, 4 H, C*H*$_2$OCH$_3$), 3.16 (s, 6 H, CH_2OCH_3), 2.50 [spt, J(HH) 7.3, 4 H, AsC*H*CH_3], 2.34 (m, 4 H, $AsCH_2$), 1.38 and 1.27 [both d, J(HH) 7.3, 24 H, AsCHC*H*$_3$], 1.10 [s, 9 H, C(CH$_3$)$_3$], 0.33 [d, J(RhH) 1.5 Hz, 1 H, =C=CH]; ^{13}C (50.3 MHz, C_6D_6), δ 288.22 [d, J(RhC) 52.1, =*C*=CH], 121.41 [d, J(RhC) 14.0 Hz, =C=*C*H], 70.21 (s, *C*H_2OCH_3), 58.06 (s, CH_2OCH_3), 32.48 [s, *C*(CH$_3$)$_3$], 25.15 [s, C(*C*H$_3$)$_3$], 25.10 (s, As*C*HCH_3), 20.91 and 19.92 (both s, AsCH*C*H_3), 19.47 (s, $AsCH_2$).

trans-[RhCl(CH_2=C=CH_2)($Pr^i_2AsCH_2CH_2OMe)_2$] **21**. Propyne (470 mg, 11.7 mmol) was condensed into a cooled Schlenk tube (−78 °C) and under stirring treated with a cooled (−40 °C) solution of **5** (78 mg, 0.13 mmol) in pentane (10 cm^3). After the reaction mixture was warmed to room temperature and stirred for 15 min, the solvent was removed *in vacuo*. The oily residue was dissolved in hexane (1 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane–benzene (1:1), a yellow fraction was eluted which was brought to dryness *in vacuo*. The remaining yellow oil was dried thoroughly *in vacuo* (10^{-3} Torr): yield 75 mg (89%) (Found: C, 41.05; H, 7.65. Calc. for $C_{21}H_{46}As_2ClO_2Rh$: C, 40.75; H, 7.50%). IR (C_6H_6), ν(C=C=C) 1724 cm^{-1}. NMR: ^{1}H (200 MHz, C_6D_6), δ 5.41 [ddt, J(RhH) 0.3, ^2J(HH) 1.4, ^4J(HH) 2.8, 1 H, H_{exo} of CH_2=C], 5.25 [ddt, J(RhH) 0.5, ^2J(HH) 1.4, ^4J(HH) 2.8, 1 H, H_{endo} of CH_2=C], 3.68 (m, 4 H, C*H*$_2$OCH$_3$), 3.16 (s, 6 H, CH_2OCH_3), 2.45 [spt, J(HH) 7.3, 2 H, AsC*H*CH_3], 2.30 [ddd, J(RhH) = $^4J(HH_{exo})$ = $^4J(HH_{endo})$ = 2.8, 2 H, η^2-C*H*$_2$=C], 2.29 [spt, J(HH) 7.1, 2 H, AsC*H*CH_3], 1.90 (m, 4 H, $AsCH_2$), 1.44 and 1.22 [both d, J(HH) 7.3, 12 H, AsCHC*H*$_3$], 1.34 and 1.18 [both d, J(HH) 7.1, 12 H, AsCHC*H*$_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 171.83 [d, J(RhC) 20.4, =C=], 95.51 [d, J(RhC) 2.8, CH_2 unco-ordinated], 69.96 (s, *C*H_2OCH_3), 58.03 (s, CH_2OCH_3), 25.04 and 24.48 (both s, As*C*HCH_3), 20.91, 20.59, 20.43 and 19.91 (all s, AsCH*C*H_3), 17.23 (s, $AsCH_2$), 6.63 [d, J(RhC) 12.0 Hz, CH_2 co-ordinated].

trans-[RhCl(CH_2=C=CHBu^t)($Pr^i_2AsCH_2CH_2OMe)_2$] **22**. A solution of **5** (75 mg, 0.12 mmol) in pentane (8 cm^3) was treated at −78 °C with 4,4-dimethylpent-2-yne (30 μl, 0.31 mmol) and, under warming to room temperature, stirred for 15 min. Further work-up was as described for **21**. A yellow oil was obtained: yield 77 mg (95%) (Found: C, 44.45; H, 7.75. Calc. for $C_{25}H_{56}As_2ClO_2Rh$: C, 44.50; H, 8.05%). IR (C_6H_6), ν(C=C=C) 1736 cm^{-1}. NMR: ^{1}H (200 MHz, C_6D_6), δ 5.57 [m, 1 H, =C*H*C(CH$_3$)$_3$], 3.64 (m, 4 H, C*H*$_2$OCH$_3$), 3.16 (s, 6 H, CH_2OCH_3), 2.45 [spt, J(HH) 7.3, 2 H, AsC*H*CH_3], 2.33 [dd, J(RhH) = ^4J(HH) = 2.7, 2 H, η^2-CH_2=C], 2.30 [spt, J(HH) 7.1, 2 H, AsC*H*CH_3], 1.86 (m, 4 H, $AsCH_2$), 1.40 and 1.22 [both d, J(HH) 7.3, 12 H, AsCHC*H*$_3$], 1.36 and 1.18 [both d, J(HH) 7.1 Hz, 12 H, AsCHC*H*$_3$], 1.14 [s, 9 H, C(CH$_3$)$_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 155.64 [d, J(RhC) 20.3, =C=], 120.09 [d, J(RhC) 1.9, =*C*HC(CH$_3$)$_3$], 69.92 (s, *C*H_2OCH_3), 58.03 (s, CH_2OCH_3), 33.37 [s, *C*(CH$_3$)$_3$], 30.41 [s, C(*C*H$_3$)$_3$], 24.56 and 24.42 (both s, As*C*HCH_3), 20.87, 20.56, 20.45 and 20.02 (all s, AsCH*C*H_3), 16.24 (s, $AsCH_2$), 9.41 [d, J(RhC) 12.0 Hz, *C*H_2=C].

trans-[RhCl(MeC≡C–C≡CMe)($Pr^i_2AsCH_2CH_2OMe)_2$] **23**. A solution of **5** (160 mg, 0.26 mmol) in pentane (15 cm^3) was treated at −78 °C with hexa-2,4-diyne (21 mg, 0.26 mmol). After the solution was warmed to −30 °C, the solvent was removed *in vacuo*. The oily residue was dissolved in hexane (2 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, an orange-yellow fraction was eluted which was brought to dryness *in vacuo*. The oily residue was recrystallized from pentane (2 cm^3) to give, after cooling to −78 °C, orange-yellow crystals which melt above 0 °C: yield 163 mg (94%) (Found: C, 43.95; H, 7.55. Calc. for $C_{24}H_{48}As_2ClO_2Rh$: C, 43.90; H, 7.35%). IR (C_6H_6), ν(C≡$C_{uncoord.}$) 2197, ν(C≡$C_{coord.}$) 1904 cm^{-1}. NMR: ^{1}H (200 MHz, C_6D_6), δ 3.84 (m, 4 H, C*H*$_2$OCH$_3$), 3.23 (s, 6 H, CH_2OCH_3), 2.35 [spt, J(HH) 7.3, 2 H, AsC*H*CH_3], 2.27 [spt, J(HH) 7.1, 2 H, AsC*H*CH_3], 2.04 (s, 3 H, $CH_3C{\equiv}C_{coord.}$), 1.95 (m, 4 H, $AsCH_2$), 1.49 (s, 3 H, $CH_3C{\equiv}C_{uncoord.}$), 1.45 and 1.33 [both d, J(HH) 7.3, 12 H, AsCHC*H*$_3$], 1.42 and 1.24 [both d, J(HH) 7.1 Hz, 12 H, AsCHC*H*$_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 84.05 (s, $CH_3C{\equiv}C_{uncoord.}$), 78.52 [d, J(RhC) 14.6, $CH_3C{\equiv}C_{coord.}$], 71.00 [d, J(RhC) 2.4, $CH_3C{\equiv}C_{uncoord.}$], 70.08 (s, *C*$H_2OCH_3$), 57.95 (s, CH_2OCH_3), 44.86 [d, J(RhC) 13.4 Hz, $CH_3C{\equiv}C_{coord.}$], 24.86 and 24.35 (both s, As*C*HCH_3), 20.79, 20.67, 20.25 and 20.01 (all s, AsCH*C*H_3), 18.68 (s, $AsCH_2$), 12.81 (s, *C*$H_3C{\equiv}C_{coord.}$), 5.24 (s, *C*$H_3C{\equiv}C_{uncoord.}$).

trans-[RhCl($Me_3SiC{\equiv}C–C{\equiv}CSiMe_3$)($Pr^i_2AsCH_2CH_2$-OMe)$_2$] **24**. A solution of **5** (61 mg, 0.10 mmol) in diethyl ether (10 cm^3) was treated at −78 °C with a solution of 1,4-bis(trimethylsilyl)buta-1,3-diyne (20 mg, 0.10 mmol) in diethyl ether (2 cm^3) and, after warming to room temperature, stirred for 15 min. The solvent was removed *in vacuo*, the oily residue was dissolved in hexane (1 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, an orange fraction was eluted which was brought to dryness *in vacuo*. The remaining orange oil was dried thoroughly *in vacuo* (10^{-3} Torr): yield 71 mg (91%) (Found: C, 43.30; H, 7.85. Calc. for $C_{28}H_{60}As_2ClO_2RhSi_2$: C, 43.50; H, 7.80%). IR (C_6H_6), ν(C≡$C_{uncoord.}$) 2120, ν(C≡$C_{coord.}$) 1828 cm^{-1}. NMR: ^{1}H (200 MHz, C_6D_6), δ 3.72 (m, 4 H, C*H*$_2$OCH$_3$), 3.22 (s, 6 H, CH_2OCH_3), 2.51 and 2.27 [both spt, J(HH) 7.2, 4 H, AsC*H*CH_3], 2.00 and 1.80 (both m, 4 H, $AsCH_2$), 1.49, 1.47, 1.41 and 1.19 [all d, J(HH) 7.2 Hz, 24 H, AsCHC*H*$_3$], 0.37 [s, 9 H, $(H_3C)_3SiC{\equiv}C_{coord.}$], 0.20 [s, 9 H, $(H_3C)_3SiC{\equiv}C_{uncoord.}$]; ^{13}C (50.3 MHz, C_6D_6), δ 100.46 and 96.49 (both s, C≡$C_{uncoord.}$), 86.67 and 83.71 [both d, J(RhC) 14.4 Hz, C≡$C_{coord.}$], 69.71 (s, *C*H_2OCH_3), 58.02 (s, CH_2OCH_3), 25.28 and 24.11 (both s, As*C*HCH_3), 21.41, 20.90, 20.79 and 19.85 (all s, AsCH*C*H_3), 17.79 and 14.23 (both s, $AsCH_2$), 0.45 and −0.38 [both s, Si(CH$_3$)$_3$].

trans-[RhCl{=C=CHC(OH)Me_2}($Pr^i_2AsCH_2CH_2OMe)_2$] **25**. A solution of **5** (83 mg, 0.14 mmol) in pentane (10 cm^3) was treated at −78 °C with 2-methylbut-3-yn-2-ol (14 μl, 0.15

mmol) and, after warming to room temperature, stirred for 10 min. A change of colour from orange-yellow to violet-brown was observed. The solvent was removed *in vacuo*, the residue was dissolved in benzene (0.5 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane–benzene (1 : 1), a violet fraction was eluted which was brought to dryness *in vacuo*. The oily residue was recrystallized from pentane (1 cm^3) to give, after cooling to −78 °C, violet crystals which melt above 0 °C: yield 81 mg (87%) (Found: C, 41.55; H, 7.70. Calc. for $C_{23}H_{50}As_2ClO_3Rh$: C, 41.70; H, 7.60%). IR (C_6H_6), ν(OH) 3445, ν(C=C) 1642 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 4.48 (br s, 1 H, OH), 3.75 (m, 4 H, CH_2OCH_3), 3.10 (s, 6 H, CH_2OCH_3), 2.47 [spt, *J*(HH) 7.2, 4 H, $AsCHCH_3$], 2.25 (m, 4 H, $AsCH_2$), 1.49 [s, 6 H, $C(OH)(CH_3)_2$], 1.37 and 1.21 [both d, *J*(HH) 7.2, 24 H, $AsCHCH_3$], 0.73 [d, *J*(RhH) 1.3 Hz, 1 H, =C=CH]; ^{13}C (50.3 MHz, C_6D_6), δ 286.81 [d, *J*(RhC) 53.5, =C=CH], 120.97 [d, *J*(RhC) 13.6 Hz, =C=CH], 69.94 (s, CH_2OCH_3), 62.31 [s, $C(OH)(CH_3)_2$], 58.02 (s, CH_2OCH_3), 32.34 [s, $C(OH)(CH_3)_2$], 25.35 (s, $AsCHCH_3$), 20.92 and 19.79 (both s, $AsCHCH_3$), 19.22 (s, $AsCH_2$).

trans-[RhCl{=C=CHC(OH)Pr^i_2}($Pr^i_2AsCH_2CH_2OMe$)$_2$] **26**. This compound was prepared as described for **25**, using **5** (73 mg, 0.12 mmol) and 3-isopropyl-4-methylpent-1-yn-3-ol (19 μl, 0.12 mmol) as starting materials. A red-violet microcrystalline solid was obtained: yield 75 mg (87%), m.p. 32 °C (decomp.) (Found: C, 45.00; H, 8.40. Calc. for $C_{27}H_{58}As_2ClO_3Rh$: C, 45.10; H, 8.15%). IR (C_6H_6), ν(OH) 3440, ν(C=C) 1650 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 3.76 (m, 4 H, CH_2OCH_3), 3.13 (s, 6 H, CH_2OCH_3), 2.89 (br s, 1 H, OH), 2.55 [spt, *J*(HH) 7.1, 4 H, $AsCHCH_3$], 2.31 (m, 4 H, $AsCH_2$), 1.89 [spt, *J*(HH) 6.8, 2 H, $C(OH)\{CH(CH_3)_2\}_2$], 1.40 and 1.25 [both d, *J*(HH) 7.1, 24 H, $AsCHCH_3$], 1.16 and 1.03 [both d, *J*(HH) 6.8, 12 H, $C(OH)\{CH(CH_3)_2\}_2$], 0.48 [d, *J*(RhH) 1.8 Hz, 1 H, =C=CH]; ^{13}C (50.3 MHz, C_6D_6), δ 286.99 [d, *J*(RhC) 54.9, =C=CH], 110.27 [d, *J*(RhC) 14.6 Hz, =C=CH], 76.26 [s, C(OH)], 70.00 (s, CH_2OCH_3), 58.07 (s, CH_2OCH_3), 25.54 (s, $AsCHCH_3$), 24.73 [s, $C(OH)\{CH(CH_3)_2\}_2$], 21.00 and 19.89 (both s, $AsCHCH_3$), 20.01 and 19.37 [both s, $C(OH)\{CH(CH_3)_2\}_2$], 17.36 (s, $AsCH_2$).

trans-[RhCl{=C=CHC(OH)Ph_2}($Pr^i_2AsCH_2CH_2OMe$)$_2$] **27**. A solution of **5** (72 mg, 0.12 mmol) in pentane (8 cm^3) was treated at −78 °C with a solution of 1,1-diphenylprop-2-yn-1-ol (25 mg, 0.12 mmol) in toluene (1 cm^3). A spontaneous change of colour from orange-yellow to yellow was observed. After the solution had been stirred at −78 °C for 5 min, the solvent was removed *in vacuo*. The oily residue, which changed its colour from yellow to violet within 2 min, was dissolved in hexane (2 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, a violet fraction was eluted which was brought to dryness *in vacuo*. The oily residue was recrystallized from pentane (1 cm^3) to give, after cooling to −78 °C, violet crystals: yield 78 mg (83%), m.p. 30 °C (decomp.) (Found: C, 50.35; H, 6.95. Calc. for $C_{33}H_{54}As_2ClO_3Rh$: C, 50.35; H, 6.90%). IR (KBr), ν(OH) 3401, ν(C=C) 1645 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 7.63–7.57 (m, 4 H, *o*-H of C_6H_5), 7.17–6.95 (m, 6 H, *m*-H and *p*-H of C_6H_5), 4.60 (br s, 1 H, OH), 3.68 (m, 4 H, CH_2OCH_3), 3.03 (s, 6 H, CH_2OCH_3), 2.40 [spt, *J*(HH) 7.2, 4 H, $AsCHCH_3$], 2.13 (m, 4 H, $AsCH_2$), 1.47 [d, *J*(RhH) 1.5, 1 H, =C=CH], 1.32 and 1.20 [both d, *J*(HH) 7.2 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 283.02 [d, *J*(RhC) 54.7, =C=CH], 149.75 (s, C^1 of C_6H_5), 128.25, 126.69 and 125.95 (all s, C^{2-6} of C_6H_5), 121.10 [d, *J*(RhC) 14.0 Hz, =C=CH], 70.06 (s, CH_2OCH_3), 68.47 [s, C(OH)], 57.76 (s, CH_2OCH_3), 25.16 (s, $AsCHCH_3$), 20.72 and 19.81 (both s, $AsCHCH_3$), 19.50 (s, $AsCH_2$).

trans-[RhCl{=C=CHC(OH)Ph(C_6H_4Me-*o*)}($Pr^i_2AsCH_2CH_2OMe$)$_2$] **28**. This compound was prepared as described for **27**, using **5** (73 mg, 0.12 mmol) and 1-phenyl-1-(*o*-tolyl)prop-2-yn-1-ol (27 mg, 0.12 mmol) as starting materials. Violet crystals were obtained: yield 83 mg (86%), m.p. 33 °C (decomp.) (Found: C, 51.15; H, 7.00. Calc. for $C_{34}H_{56}As_2ClO_3Rh$: C, 51.00; H, 7.05%). IR (KBr), ν(OH) 3398, ν(C=C) 1645 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 8.06–7.98 (m, 3 H, *o*-H of C_6H_5 and *o*-$C_6H_4CH_3$), 7.48–7.43 (m, 2 H, *p*-H of C_6H_5 and *o*-$C_6H_4CH_3$), 7.17–6.96 (m, 4 H, *m*-H of C_6H_5 and *o*-$C_6H_4CH_3$), 4.54 (br s, 1 H, OH), 3.71 (m, 4 H, CH_2OCH_3), 3.00 (s, 6 H, CH_2OCH_3), 2.47 and 2.38 [both spt, *J*(HH) 7.2, 4 H, $AsCHCH_3$], 2.21 (m, 4 H, $AsCH_2$), 2.16 (s, 3 H, *o*-$C_6H_4CH_3$), 1.40 [d, *J*(RhH) 1.4, 1 H, =C=CH], 1.36, 1.30, 1.27 and 1.20 [all d, *J*(HH) 7.2 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 283.54 [d, *J*(RhC) 54.8, =C=CH], 149.00 and 146.32 (both s, C^1 of C_6H_5 and *o*-$C_6H_4CH_3$), 137.20, 132.72, 127.88, 127.52, 126.44, 125.82, 125.81 and 124.88 (all s, C^{2-6} of C_6H_5 and *o*-$C_6H_4CH_3$), 122.35 [d, *J*(RhC) 13.7 Hz, =C=CH], 70.16 (s, CH_2OCH_3), 69.91 [s, C(OH)], 57.68 (s, CH_2OCH_3), 25.27 and 25.16 (both s, $AsCHCH_3$), 21.52 (s, *o*-$C_6H_4CH_3$), 20.89, 20.73, 19.99 and 19.90 (all s, $AsCHCH_3$), 19.64 (s, $AsCH_2$).

trans-[RhCl(=C=C=CPh_2)($Pr^i_2AsCH_2CH_2OMe$)$_2$] **29**. A solution of **27** (60 mg, 0.08 mmol) in hexane (2 cm^3) was chromatographed on Al_2O_3 (neutral, activity grade I, height of column 3 cm). With benzene, a deep-red fraction was eluted which was brought to dryness *in vacuo*. The oily residue was dissolved in benzene (0.5 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane–benzene (1 : 1) a red fraction was eluted which was brought to dryness *in vacuo*. The oily residue was recrystallized from pentane (2 cm^3) to give, after cooling to −78 °C, a red solid: yield 49 mg (79%), m.p. 55 °C (decomp.) (Found: C, 51.55; H, 6.70. Calc. for $C_{33}H_{52}As_2ClO_2Rh$: C, 51.55; H, 6.80%). IR (KBr), ν(C=C=C) 1875 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 7.97 [dd, ^3J(HH) 7.3, ^4J(HH) 1.3, 4 H, *o*-H of C_6H_5], 7.53–7.46 (m, 4 H, *m*-H of C_6H_5), 6.87–6.79 (m, 2 H, *p*-H of C_6H_5), 3.82 (m, 4 H, CH_2OCH_3), 3.07 (s, 6 H, CH_2OCH_3), 2.47 [spt, *J*(HH) 7.1, 4 H, $AsCHCH_3$], 2.43 (m, 4 H, $AsCH_2$), 1.33 and 1.26 [both d, *J*(HH) 7.1 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 248.35 [d, *J*(RhC) 13.4, =C=C=C], 220.25 [d, *J*(RhC) 58.6 Hz, =C=C=C], 154.32 (s, =C=C=C), 140.88 (s, C^1 of C_6H_5), 130.01, 127.20 and 124.14 (all s, C^{2-6} of C_6H_5), 70.56 (s, CH_2OCH_3), 57.95 (s, CH_2OCH_3), 25.34 (s, $AsCHCH_3$), 20.78 and 19.74 (both s, $AsCHCH_3$), 19.94 (s, $AsCH_2$).

trans-[RhCl{=C=C=CPh(C_6H_4Me-*o*)}($Pr^i_2AsCH_2CH_2OMe$)$_2$] **30**. This compound was prepared as described for **29**, using **28** (83 mg, 0.10 mmol) as the starting material. A red solid was obtained: yield 72 mg (89%), m.p. 40 °C (decomp.) (Found: C, 52.30; H, 7.15. Calc. for $C_{34}H_{54}As_2ClO_2Rh$: C, 52.15; H, 6.95%). IR (KBr), ν(C=C=C) 1877 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 8.24 [dd, ^3J(HH) 8.5, ^4J(HH) 1.1, 2 H, *o*-H of C_6H_5], 7.76 [dd, ^3J(HH) 7.4, ^4J(HH) 0.7, 1 H, *o*-H of *o*-$C_6H_4CH_3$], 7.22–7.02 (m, 4 H, *p*-H of C_6H_5 and *o*-$C_6H_4CH_3$, *m*-H of *o*-$C_6H_4CH_3$), 6.78 [dd, ^3J(HH) 7.5, 2 H, *m*-H of C_6H_5], 3.83 (m, 4 H, CH_2OCH_3), 3.10 (s, 6 H, CH_2OCH_3), 2.44 (m, 4 H, $AsCH_2$), 2.40 [spt, *J*(HH) 7.2, 4 H, $AsCHCH_3$], 2.04 (s, 3 H, *o*-$C_6H_4CH_3$), 1.30 and 1.24 [both d, *J*(HH) 7.2 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 246.94 [d, *J*(RhC) 13.4, =C=C=C], 221.51 [d, *J*(RhC) 58.8 Hz, =C=C=C], 153.62 (s, =C=C=C), 143.14 and 141.78 (both s, C^1 of C_6H_5 and *o*-$C_6H_4CH_3$), 131.17, 130.52, 130.26, 127.53, 124.83, 124.72 and 120.17 (all s, C^{2-6} of C_6H_5 and *o*-$C_6H_4CH_3$), 70.59 (s, CH_2OCH_3), 58.04 (s, CH_2OCH_3), 25.28 (s, $AsCHCH_3$), 20.31 (s, *o*-$C_6H_4CH_3$), 20.74 and 19.76 (both s, $AsCHCH_3$), 20.01 (s, $AsCH_2$).

[Rh(C_5H_5)(=C=C=CPh_2)($Pr^i_2AsCH_2CH_2OMe$)] **31**. A solution of **29** (77 mg, 0.10 mmol) in thf (10 cm^3) was treated at room temperature with NaC_5H_5 (44 mg, 0.50 mmol) and stirred for 30 min. A spontaneous change of colour from red to green-blue was observed. The solvent was removed *in vacuo*, the oily residue was extracted twice with pentane (10 cm^3 each), and the combined extracts were brought to dryness *in vacuo*. The residue was dissolved in hexane (1 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade IV, height of column 3 cm). With hexane, a turquoise fraction was eluted

which was brought to dryness *in vacuo*. The remaining oil was dried thoroughly *in vacuo* (10^{-3} Torr): yield 38 mg (66%) (Found: C, 60.50; H, 6.10. Calc. for $C_{29}H_{36}AsORh$: C, 60.20; H, 6.25%). MS (70 eV) 578 (M^+). IR (C_6H_6), ν(C=C=C) 1908 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 7.71–7.66 (m, 4 H, *o*-H of C_6H_5), 7.14–6.95 (m, 6 H, *m*-H and *p*-H of C_6H_5), 5.02 [d, *J*(RhH) 0.7, 5 H, C_5H_5], 3.46 (m, 2 H, CH_2OCH_3), 2.97 (s, 3 H, CH_2OCH_3), 1.90 [spt, *J*(HH) 7.2, 2 H, $AsCHCH_3$], 1.53 (m, 2 H, $AsCH_2$), 0.98 and 0.95 [both d, *J*(HH) 7.2 Hz, 12 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 225.73 [d, *J*(RhC) 68.4, =C=C=C], 209.25 [d, *J*(RhC) 15.9, =C=C=C], 165.33 (s, =C=C=C), 149.39 (s, C^1 of C_6H_5), 132.03, 130.18 and 126.08 (all s, C^{2-6} of C_6H_5), 81.50 [d, *J*(RhC) 4.9 Hz, C_5H_5], 70.53 (s, CH_2OCH_3), 58.02 (s, CH_2OCH_3), 26.75 (s, $AsCHCH_3$), 19.52 and 19.40 (both s, $AsCHCH_3$), 18.79 (s, $AsCH_2$).

$[Rh(C_5H_5)\{=C=C=CPh(C_6H_4Me\text{-}o)\}(Pr^i_2AsCH_2CH_2OMe)]$ **32**. This compound was prepared as described for **31**, using **30** (94 mg, 0.12 mmol) and NaC_5H_5 (53 mg, 0.60 mmol) as starting materials. A turquoise-blue oil was obtained: yield 48 mg (68%) (Found: C, 61.00; H, 6.30. Calc. for $C_{30}H_{38}AsORh$: C, 60.80; H, 6.45%). MS (70 eV) 592 (M^+). IR (C_6H_6), ν(C=C=C) 1912 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 8.56–8.53 (m, 1 H, *o*-H of *o*-$C_6H_4CH_3$), 8.23–8.19 (m, 2 H, *o*-H of C_6H_5), 7.26–6.95 (m, 6 H, *m*-H and *p*-H of C_6H_5 and *o*-$C_6H_4CH_3$), 5.01 [d, *J*(RhH) 0.7, 5 H, C_5H_5], 3.45 (m, 2 H, CH_2OCH_3), 3.03 (s, 3 H, CH_2OCH_3), 2.26 [spt, *J*(HH) 7.2, 2 H, $AsCHCH_3$], 2.17 (s, 3 H, *o*-$C_6H_4CH_3$), 1.59 (m, 2 H, $AsCH_2$), 0.96 and 0.93 [both d, *J*(HH) 7.2 Hz, 12 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 227.52 [d, *J*(RhC) 67.7, =C=C=C], 207.85 [d, *J*(RhC) 16.0, =C=C=C], 163.18 (s, =C=C=C), 147.10 and 146.84 (both s, C^1 of C_6H_5 and *o*-$C_6H_4CH_3$), 135.98 (s, C^2 of *o*-$C_6H_4CH_3$), 133.59, 130.32, 129.97, 127.76, 126.85, 126.21 and 125.49 (all s, C^{2-6} of C_6H_5 and C^{3-6} of *o*-$C_6H_4CH_3$), 81.51 [d, *J*(RhC) 4.3 Hz, C_5H_5], 70.53 (s, CH_2OCH_3), 58.11 (s, CH_2OCH_3), 26.30 (s, $AsCHCH_3$), 22.77 (s, *o*-$C_6H_4CH_3$), 19.64 and 19.05 (both s, $AsCHCH_3$), 14.23 (s, $AsCH_2$).

trans-$[RhCl(=CPh_2)(Pr^i_2AsCH_2CH_2OMe)_2]$ **33**. A solution of **5** (169 mg, 0.28 mmol) in pentane (12 cm^3) was treated at −78 °C with a solution of diphenyldiazomethane (119 mg, 0.60 mmol) in pentane (3 cm^3). After warming to room temperature the solution was stirred under reduced pressure (≈50 Torr) for 15 min. The brown-green reaction mixture was then concentrated to 1 cm^3 *in vacuo*, and the concentrate was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, first a violet fraction was eluted which contained the excess of diphenyldiazomethane. The second brown-green fraction was brought to dryness *in vacuo*, the oily residue was dissolved in benzene (0.5 cm^3), and the solution was either stirred at room temperature for 5 h or irradiated with UV light for 20 min. After the solvent was removed, the oily residue was dissolved in hexane (1 cm^3), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, a yellow-green fraction was eluted which after removal of the solvent gave an oily residue that was recrystallized from pentane (2 cm^3) to give, after cooling to −78 °C, a green-yellow solid which melts above 10 °C: yield 63 mg (30%) (Found: C, 50.05; H, 6.80. Calc. for $C_{31}H_{52}As_2ClO_2Rh$: C, 50.00; H, 7.05%). NMR: ^1H (200 MHz, C_6D_6), δ 7.97 [dd, ^3J(HH) 7.1, ^4J(HH) 1.1, 4 H, *o*-H of C_6H_5], 7.11–6.90 (m, 6 H, *m*-H and *p*-H of C_6H_5), 3.64 (m, 4 H, CH_2OCH_3), 3.13 (s, 6 H, CH_2OCH_3), 2.15 [spt, *J*(HH) 7.2, 4 H, $AsCHCH_3$], 1.80 (m, 4 H, $AsCH_2$), 1.28 [d, *J*(HH) 7.1, 12 H, $AsCHCH_3$], 1.08 [d, *J*(HH) 7.3 Hz, 12 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 313.76 [d, *J*(RhC) 33.0 Hz, Rh=C], 159.91 (s, C^1 of C_6H_5), 131.71, 130.10 and 129.74 (all s, C^{2-6} of C_6H_5), 70.42 (s, CH_2OCH_3), 57.91 (s, CH_2OCH_3), 25.62 (s, $AsCHCH_3$), 21.07 and 19.98 (both s, $AsCHCH_3$), 20.13 (s, $AsCH_2$).

trans-$[RhCl\{=C(C_6H_4Me\text{-}p)_2\}(Pr^i_2AsCH_2CH_2OMe)_2]$ **34**. This compound was prepared as described for **33**, using **5** (180 mg, 0.30 mmol) and di(*p*-tolyl)diazomethane (132 mg, 0.60 mmol) as starting materials. A bright green oil was obtained: yield 142 mg (61%) (Found: C, 51.00; H, 7.45. Calc. for $C_{33}H_{56}As_2ClO_2Rh$: C, 51.30; H, 7.30%). NMR: ^1H (200 MHz, C_6D_6), δ 7.94 [d, ^3J(HH) 8.1, 4 H, *o*-H of $C_6H_4CH_3$], 6.98 [d, ^3J(HH) 8.1, 4 H, *m*-H of $C_6H_4CH_3$], 3.66 (m, 4 H, CH_2OCH_3), 3.14 (s, 6 H, CH_2OCH_3), 2.15 [spt, *J*(HH) 7.3, 4 H, $AsCHCH_3$], 1.80 (m, 4 H, $AsCH_2$), 1.77 (s, 6 H, $C_6H_4CH_3$), 1.28 and 1.06 [both d, *J*(HH) 7.3 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 314.51 [d, *J*(RhC) 32.0 Hz, Rh=C], 158.47 (s, C^1 of $C_6H_4CH_3$), 135.99, 130.38 and 129.04 (all s, $C_6H_4CH_3$), 70.56 (s, CH_2OCH_3), 57.97 (s, CH_2OCH_3), 25.63 (s, $AsCHCH_3$), 21.83 (s, $C_6H_4CH_3$), 21.35 and 21.14 (both s, $AsCHCH_3$), 20.10 (s, $AsCH_2$).

trans-$[RhCl\{N_2CHC(O)Ph\}(Pr^i_2AsCH_2CH_2OMe)_2]$ **35**. A solution of **5** (74 mg, 0.12 mmol) in pentane (10 cm^3) was treated at −78 °C with benzoylidiazomethane (18 mg, 0.12 mmol) and after warming to room temperature stirred for 15 min. A gradual change of colour from yellow to red was observed. The solvent was removed *in vacuo*, the residue was washed twice with small amounts of pentane (−40 °C) and recrystallized from pentane (5 cm^3) to give, after cooling to −78 °C, a red crystalline solid: yield 77 mg (88%), m.p. 33 °C (decomp.) (Found: C, 42.90; H, 6.75; N, 3.70. Calc. for $C_{26}H_{48}As_2ClN_2O_3Rh$: C, 43.10; H, 6.65; N, 3.85%). IR (C_6H_6), ν(N_2) 1931, ν(C=O) 1628 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 7.85–7.80 (m, 2 H, *o*-H of C_6H_5), 7.33–7.10 (m, 3 H, *m*-H and *p*-H of C_6H_5), 3.64 (m, 4 H, CH_2OCH_3), 3.13 (br s, 1 H, N_2CH), 3.06 (s, 6 H, CH_2OCH_3), 2.51 and 2.22 [both spt, *J*(HH) 7.0, 4 H, $AsCHCH_3$], 2.05 (m, 4 H, $AsCH_2$), 1.32, 1.25, 1.17 and 1.16 [all d, *J*(HH) 7.0 Hz, 24 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 149.60 [s, C(O)], 136.29 (s, C^1 of C_6H_5), 129.49, 128.12 and 126.61 (all s, C^{2-6} of C_6H_5), 83.06 (d, *J*(RhC) 3.8 Hz, N_2C], 69.18 (s, CH_2OCH_3), 57.83 (s, CH_2OCH_3), 25.59 and 24.51 (both s, $AsCHCH_3$), 20.16, 19.93, 19.76 and 19.43 (all s, $AsCHCH_3$), 19.07 (s, $AsCH_2$).

trans-$[RhCl\{N_2CPhC(O)Ph\}(Pr^i_2AsCH_2CH_2OMe)_2]$ **36**. This compound was prepared as described for **35**, using **5** (82 mg, 0.14 mmol) and benzoyl(phenyl)diazomethane (30 mg, 0.14 mmol) as starting materials. A red crystalline solid was obtained: yield 87 mg (31%), m.p. 31 °C (decomp.) (Found: C, 47.95; H, 6.70; N, 3.30. Calc. for $C_{32}H_{52}As_2ClN_2O_3Rh$: C, 48.00; H, 6.55; N, 3.50%). IR (C_6H_6), ν(N_2) 1923, ν(C=O) 1603 cm^{-1}. NMR: ^1H (200 MHz, C_6D_6), δ 7.58–7.41 (m, 4 H, *o*-H of C_6H_5), 7.16–6.94 (m, 6 H, *m*-H and *p*-H of C_6H_5), 3.66 (m, 4 H, CH_2OCH_3), 3.08 (s, 6 H, CH_2OCH_3), 2.57 [spt, *J*(HH) 7.3, 2 H, $AsCHCH_3$], 2.25 [spt, *J*(HH) 7.1, 2 H, $AsCHCH_3$], 2.12 (m, 4 H, $AsCH_2$), 1.34 and 1.21 [both d, *J*(HH) 7.3, 12 H, $AsCHCH_3$], 1.28 and 1.17 [both d, *J*(HH) 7.1 Hz, 12 H, $AsCHCH_3$]; ^{13}C (50.3 MHz, C_6D_6), δ 151.60 [s, C(O)], 139.12 and 137.96 (both s, C^1 of C_6H_5), 130.26, 129.69, 128.62, 127.78, 125.39 and 124.95 (all s, C^{2-6} of C_6H_5), 101.09 [d, *J*(RhC) 1.9 Hz, N_2C], 69.21 (s, CH_2OCH_3), 58.01 (s, CH_2OCH_3), 25.67 and 24.42 (both s, $AsCHCH_3$), 20.23, 19.88, 19.82 and 19.33 (all s, $AsCHCH_3$), 19.16 (s, $AsCH_2$).

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