Synthesis of $[(C_5H_5)Rh(\eta^3\text{-}1\text{-}MeC_3H_4)(P\text{-}i\text{-}Pr_3)]PF_6$ from $(C_5H_5)Rh(MeC{\equiv}CMe)(P\text{-}i\text{-}Pr_3)$. The Mechanism of Conversion of an Alkyne into an Allyl Ligand via an Allene Intermediate[1]

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The but-2-yne compound $(C_5H_5)Rh(MeC{\equiv}CMe)(P\text{-}i\text{-}Pr_3)$ (**3**), prepared from *trans*-$[RhCl(MeC{\equiv}CMe)(P\text{-}i\text{-}Pr_3)_2]$ (**2**) and NaC_5H_5 in 63% yield, reacts with Brønsted acids, HX, to form salts of the (1-methylallyl)rhodium cation $[(C_5H_5)Rh(C_4H_7)(P\text{-}i\text{-}Pr_3)]^+$. The conversion of the alkyne to the 1-methylallyl unit occurs via the vinylmetal cation $[(C_5H_5)Rh((E)\text{-}CH_3C{=}CHCH_3)(P\text{-}i\text{-}Pr_3)]^+$ (**8**) which in the presence of iodide can be trapped to produce the iodo derivative **11**. In absence of I^-, **8** rearranges to give the isomeric (allene)hydridorhodium cation **9** from which the neutral allene complex $(C_5H_5)Rh(\eta^2\text{-}CH_2{=}C{=}CHCH_3)(P\text{-}i\text{-}Pr_3)$ (**12**) can be obtained. Protonation of **12** with HBF_4 in ether followed by metathesis with NH_4PF_6 also gives the 1-methylallyl compound *t,a*-**5c**, whereas the reaction of **12** with CF_3CO_2H in the presence of iodide produces the vinylrhodium derivative **11**. Deuteriation experiments have also confirmed that an allene rhodium complex is formed as an intermediate during the conversion of but-2-yne into the 1-methylallyl ligand of **5**.

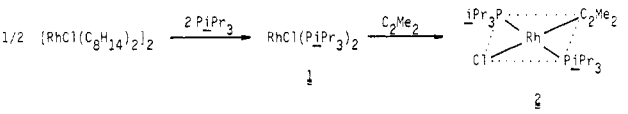
Introduction

Following the discovery that the half-sandwich-type complexes $(C_5H_5)Rh(PR_3)_2$ (PR_3 = PMe_3,[2] P-*i*-Pr_3[3]) are strong *metal bases*,[4,5] we became interested in determining whether this nucleophilic behavior is still retained when one of the phosphines is substituted by a better π-acceptor ligand such as CO, C_2H_4, etc. During the course of these investigations we observed that not only are the olefin compounds $(C_5H_5)Rh(C_2H_3R)(PMe_3)$ (R = H, Me, Ph) easily protonated and alkylated[6] but also the cationic products obtained on protonation possess interesting dynamic properties. By means of NMR measurements and labeling studies it has been shown that the hydrido olefin cations $[(C_5H_5)RhH(C_2H_3R)(PMe_3)]^+$ in solution are in rapid equilibrium with the (possibly solvated) alkyl isomers which for R = Ph further rearrange to form the thermodynamically prefered π-allyl derivative $[(C_5H_5)Rh(\eta^3\text{-}CHMeC_6H_5)(PMe_3)]^+$. The structure of the PF_6 salt of this cation has been confirmed by X-ray analysis.[7]

In a continuation of these studies, we decided to prepare the alkyne analogues of the olefin phosphine complexes and to explore their nucleophilic properties. By doing this, we not only found a convenient and widely applicable route to (vinylidene)rhodium compounds $(C_5H_5)Rh(=C=CHR)(P\text{-}i\text{-}Pr_3)$[8,9] but also discovered that the alkyne hydrido cations $[(C_5H_5)RhH(PhC{\equiv}CR)(P\text{-}i\text{-}Pr_3)]^+$ (R = H, Ph), provided that they are formed from $(C_5H_5)Rh(PhC{\equiv}CR)(P\text{-}i\text{-}Pr_3)$ and HX in the primary step, rapidly rearrange to produce either vinylrhodium complexes or metallaheterocycles.[10] The behavior of the corresponding but-2-yne compound $(C_5H_5)Rh(MeC{\equiv}CMe)(P\text{-}i\text{-}Pr_3)$ as well as the elucidation of the mechanism of its protonation reaction is reported in this paper. A short communication describing some preliminary results has already appeared.[11]

Results and Discussion

Synthesis and Reactivity of $(C_5H_5)Rh(C_2Me_2)(P\text{-}i\text{-}Pr_3)$ (3). The monomeric 14-electron species $RhCl(P\text{-}i\text{-}Pr_3)_2$ (**1**), which is formed from the chloro-bridged dimer $[RhCl(C_8H_{14})_2]_2$ and excess of triisopropylphosphine,[12] reacts with but-2-yne to produce *trans*-$[RhCl(C_2Me_2)(P\text{-}i\text{-}Pr_3)_2]$ (**2**) in 63% yield. It is recommended not to isolate the coordinatively unsaturated, extremely air-sensitive complex **1** but to treat it directly in pentane with the alkyne. **2** forms orange-red crystals that are moderately stable under nitrogen in the solid state but slowly decompose in solution.



The trans configuration of the square-planar compound **2** is confirmed by its ^1H NMR spectrum. The methyl protons of the triisopropylphosphine ligands form a doublet of virtual triplets that is expected for a linear P-*i*-Pr_3–M–P-*i*-Pr_3 arrangement.[13] In the IR spectrum of **2** the C≡C stretching frequency occurs at 1950 cm^{-1} (KBr) and is lowered by 283 cm^{-1} compared to free but-2-yne. Such a difference has also been found between C_2Ph_2 and *trans*-$[RhCl(C_2Ph_2)(P\text{-}i\text{-}Pr_3)_2]$[10] and seems to be typical for π-bonded two-electron alkyne ligands.[14]

The reaction of **2** with NaC_5H_5 in tetrahydrofuran gives the half-sandwich-type complex **3** in good yield. The yellow crystalline compound is remarkably stable and easily soluble in most organic solvents. The composition is confirmed by both elemental analysis and mass spectroscopy. Treatment of **3** with methyl iodide in nitromethane at room temperature leads to complete displacement of the alkyne ligand and almost quantitative formation of $(C_5H_5)RhCH_3(P\text{-}i\text{-}Pr_3)I$ (**4**). This complex has previously been obtained from $(C_5H_5)Rh(P\text{-}i\text{-}Pr_3)_2$ and

(1) Part 61 of the series "Basic Metals". Part 60: Werner, H.; Hofmann, L.; Zolk, R. *Chem. Ber.* **1987**, *120*, 379.
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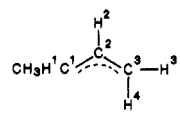
Table I. ^1H and ^{13}C NMR Data of Compounds *t,a*-5c and *t,s*-5c in CD_3NO_2[a]

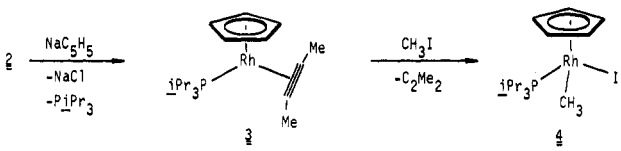
	^1H NMR					^{13}C NMR					
	t,a-5c		*t,s*-5c			*t,a*-5c			*t,s*-5c		
	δ	*J*(HH)	δ	*J*(HH)		δ	*J*(PC)	*J*(RhC)	δ	*J*(PC)	*J*(RhC)
$PCHCH_3$[b]	1.26 (dd)[c]	6.6	1.35 (dd)[d]	8.0	$PCHCH_3$	19.88 (s)			19.98 (s)		
$PCHCH_3$	2.28 (m)		2.32 (m)			20.04 (s)			20.37 (s)		
CH_3	1.38 (d)	6.6	1.87 (d)	5.8	$PCHCH_3$	28.64 (d)	21.3		28.42 (d)	23.5	
H^4	3.78 (d)	12.8	*e*		CH_3	20.63 (s)			22.38 (s)		
H^3	4.09 (d)	7.4	3.89 (d)	7.0	C^3	45.45 (d)		8.8	43.04 (dd)	3.7	11.0
H^2	4.52 (m)		5.31 (m)		C^2	94.75 (d)		5.1	82.89 (dd)	1.5	5.1
H^1	5.21 (m)		3.02 (m)		C^1	71.32 (dd)	1.5	9.6	71.08 (dd)	2.9	9.6
C_5H_5	5.68 (dd)[f]		5.72 (dd)[g]		C_5H_5	94.36 (dd)	2.2	4.4	91.48 (dd)	1.5	4.4

[a] Assignment according to



25 °C; δ, internal $SiMe_4$; *J* in Hz; ^1H, 100 MHz, ^{13}C, 90 MHz. [b] For the diastereotopic methyl groups of the P-*i*-Pr_3 ligand two signals would be expected (see ^{13}C NMR); they are not observed because the difference in chemical shift obviously is too small. [c] *J*(PH) = 14.0 Hz. [d] *J*(PH) = 13.6 Hz. [e] Signal not observed probably due to overlap with the phosphine protons. [f] *J*(PH) = 1.5 and *J*(RhH) = 0.6 Hz. [g] *J*(PH) = 1.1 and *J*(RhH) = 0.6 Hz.

CH_3I but could not be completely separated from the phosphonium salt [P-*i*-Pr_3Me]I that is formed as a by-product in this reaction.[3]



The but-2-yne compound **3** reacts with acids such as CF_3CO_2H, HBF_4 and even NH_4PF_6 to form salts of the analytical composition $[(C_5H_5)Rh(C_4H_7)(P\text{-}i\text{-}Pr_3)]X$ (**5a–c**). The PF_6 salt **5c**, which owing to its greater stability has been used for most of the spectroscopic studies, is also obtained by a metathesis reaction from **5a** or **5b** and NH_4PF_6. It forms yellow, moderately air-stable crystals that are soluble in polar solvents and show (in nitromethane) the conductivity of a 1:1 electrolyte.

The $[(C_5H_5)Rh(C_4H_7)(P\text{-}i\text{-}Pr_3]^+$ cation, however, is not an alkyne hydrido but rather is a (η^3-1-methylallyl)rhodium complex. The NMR characteristics of the allyl protons H^1–H^4 and the carbon atoms C^1–C^3 are rather similar to those of other π-bonded (1-methylallyl)metal compounds that contain cobalt,[15] rhodium,[16] or ruthenium[17] as the central atom. As a detailed discussion of the NMR data shows, the primary product obtained in the reaction of **3** with HX in presence of PF_6^- presumably is the transoid, anti complex *t,a*-**5c** that in nitromethane slowly rearranges to give the more stable transoid,syn isomer *t,s*-**5c** (Scheme I). Both compounds that are very similar in their physical properties (color, solubility, etc.) can be best differentiated by the chemical shift of the $CHCH_3$ protons of the 1-methylallyl ligand (see Table I). Thus, in the ^1H NMR spectrum of *t,a*-**5c** the doublet of the methyl group appears at higher fields (δ 1.38) than in the spectrum of *t,s*-**5c** (δ 1.87), whereas the signal of the CH proton is observed at significantly lower fields for *t,a*-**5c** (δ 5.21) compared with that for *t,s*-**5c** (δ 3.02). This assignment agrees with the general rule that a substituent in the anti position is more shielded by the transition metal than that in the syn position.[18]

Scheme I

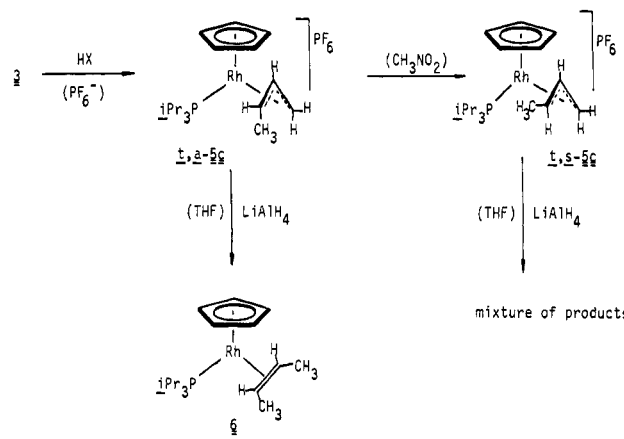
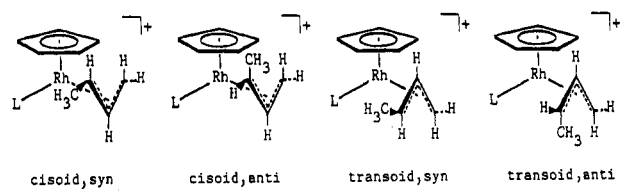


Chart I



cisoid,syn cisoid,anti transoid,syn transoid,anti

In this context, it should be mentioned that in a cation of general composition $[(C_5H_5)Rh(\eta^3\text{-}1\text{-}CH_3C_3H_4)L]^+$ four different arrangements of the 1-methylallyl group with regard to the $(C_5H_5)(L)Rh$ fragment are possible (Chart I) which are classified as cisoid,syn, cisoid,anti, transoid,syn, and transoid,anti, respectively. Whereas the syn,anti nomenclature follows established rules,[19] the cisoid, term relates to the position of the central CH unit with regard to the ligand L. According to previous results, 1-substituted allyl complexes having a cisoid conformation or an anti configuration are thermodynamically unstable compared to the transoid or the syn isomers, respectively.[17,20,21]

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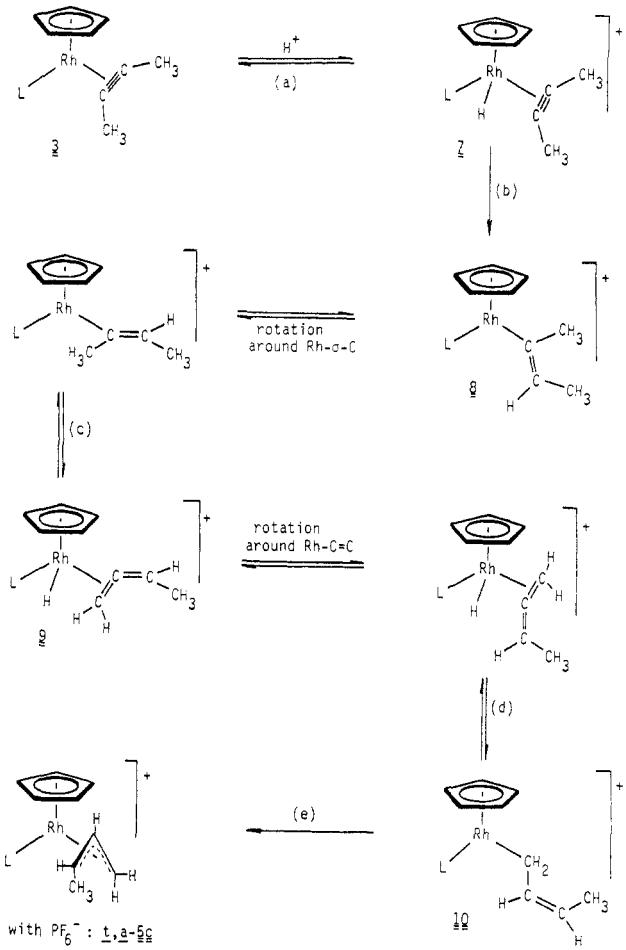
Scheme II[a]

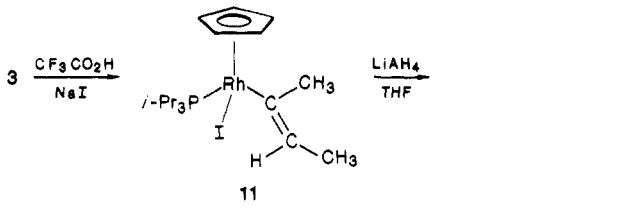


L = P-*i*-Pr$_3$

The transoid,*anti* isomer *t,a*-**5c** reacts smoothly with $LiAlH_4$ in THF to produce the neutral compound **6** which contains an *cis*-but-2-ene ligand. In contrast, the analogous reaction of *t,s*-**5c** gives a mixture of products that could not be separated by column chromatography and could not definitely be characterized by NMR spectroscopy. It is worth mentioning that other transition metals also prefer to coordinate to *cis*-but-2-ene and not to *trans*-but-2-ene.[22]

Mechanistic Studies. The formation of the 1-methylallyl group in **5** by addition of a proton to the alkyne ligand in **3** is an unexpected result, and, as far as we know, there is no precedence for this. During the conversion of $CH_3C{\equiv}CCH_3$ to $CH_3CHCHCH_2$, one C—H bond is broken and two new C—H bonds are formed, and thus the question arises how this occurs. From our recent investigations on the protonation of the olefin complexes $C_5H_5Rh(C_2H_3R)PMe_3$,[6] we assume (see Scheme II) that in the reaction of **3** with HX the first step **a** also involves attack of the proton at the metal leading to the formation of the (alkyne)hydridometal cation **7**. This primary intermediate rapidly rearranges to produce the vinylrhodium isomer **8** (step **b**) which via a β-hydride elimination gives the hydrido 1-methylallene species **9** (step **c**). Complex **9**, which can be considered as an analogue of the hydrido olefin cations $[(C_5H_5)RhH(C_2H_3R)(PMe_3)]^+$,[6] probably reacts via the σ-allyl intermediate **10** (step **d**) to form the isolated product *t,a*-**5c** (step **e**). Support for the assumption that a vinyl ligand such as in **8** can rearrange to produce a 1-methylallyl group stems from previous work by Schwartz et al., who observed that the iridium complex *trans*-$[Ir((Z)\text{-}CCH_3{=}CHCH_3)(CO)(PPh_3)_2]$ reacts on warming in C_6D_6 in a sealed tube to give the allyl isomer $[Ir(\eta^3\text{-}syn\text{-}1\text{-}CH_3C_3H_4)(CO)(PPh_3)_2]$.[23] In the reaction of $[(C_5H_5)Mo(CH_3C{\equiv}CCH_3)LL']BF_4$ (L = L' = $P(OMe)_3$; L = CO, L' = PEt_3) with hydride donors a σ-vinyl intermediate is also formed which rearranges to the corresponding (η^3-1-methylallyl)molybdenum compound.[24]

Evidence for the formation of the intermediate **8** (see Scheme II) is provided by the isolation of **11** when the reaction of **3** with CF_3CO_2H is carried out in presence of NaI. The new vinyl complex, characterized by elemental analysis and NMR spectroscopic data, forms red-brown, air-sensitive crystals that are stable even in acetone or nitromethane solution. The fact that the two methyl groups on the C=C double bond are in cis position to each other is proved by the reaction of **11** with $LiAlH_4$ in THF which gives mainly the *cis*-but-2-ene complex **6**. The dihydridorhodium compound $(C_5H_5)RhH_2(P\text{-}i\text{-}Pr_3)$[12] is also obtained as a minor product.



The rearrangement of the vinyl intermediate **8** to give an 1-methylallene complex has also been confirmed. If the reaction of **3** with NH_4PF_6 in CD_3NO_2 is monitored by ^1H NMR, it is observed that after ca. 2 min (at 35 °C) the starting material has completely disappeared and two new compounds are formed. Both are quantitatively converted in ca. 45 min to *t,a*-**5c**. The ^1H NMR spectrum of one of the intermediates[25] closely resembles that of **11** (see Experimental Section), indicating that this species presumably is the cationic vinyl complex **8**, possibly stabilized by coordination of one CD_3NO_2 molecule.

The second intermediate has been isolated. After rapid removal of the solvent and extraction of the residue with pentane, a yellow oil is obtained which according to the ^1H and ^{13}C NMR data (see Experimental Section) is the methylallene complex **12**. We suppose that it is formed from **9** and that NH_3 (the corresponding base of the weak acid NH_4^+ used for generating **9** from **3**) is responsible for the deprotonation of the hydrido(methylallene)rhodium cation.

This route, however, gives only small amounts of **12**. The complex is obtained in considerably higher yields if a hexane solution of **3** is chromatographed on deactivated Al_2O_3 by using a relatively long column. The obvious assumption that the isomerization is initiated by the acid/base couple H_2O/OH^- is strongly supported by the fact that after chromatography on Al_2O_3 which was deactivated with D_2O only the deuteriated compound $(C_5H_5)Rh(\eta^2\text{-}(E)\text{-}CH_2{=}C{=}CDCH_3)(P\text{-}i\text{-}Pr_3)$ (**12**-d_1) is produced. A very similar conversion of an alkyne into an isomeric allene ligand has recently also been observed by Richards and co-workers,[26] who obtained the complex

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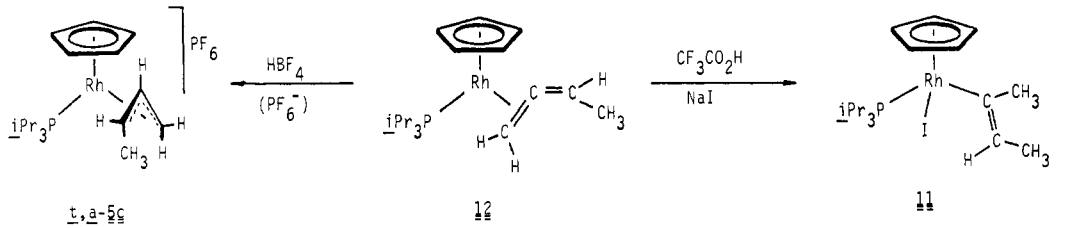
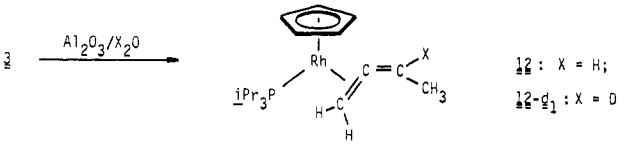
(25) ^1H NMR (CD_3NO_2): δ 5.53 (dd, *J*(PH) = 1.6 Hz, *J*(RhH) = 0.5 Hz, C_5H_5), 2.02 (s, br, CCH_3), 1.78 (d, *J*(HH) = 6.6 Hz, $CHCH_3$); signal of C*H* proton not exactly located.



t,a-5c 12 11 (1)

$ReCl(\eta^2\text{-}CH_2{=}C{=}CHPh)(diphos)_2$ from *trans*-$[ReCl(N_2)(diphos)_2]$ (diphos = $Ph_2PCH_2CH_2PPh_2$) and $PhC{\equiv}CCH_3$.



The *Z* isomer of **12**, $(C_5H_5)Rh(\eta^2\text{-}(Z)\text{-}CH_2{=}C{=}CHCH_3)(P\text{-}i\text{-}Pr_3)$, has also been characterized.[27] It is prepared from $(C_5H_5)Rh(=C{=}CHMe)(P\text{-}i\text{-}Pr_3)$ and diazomethane in the presence of the Cu^{2+} ion, i.e., by addition of CH_2 to the nucleophilic Rh=C bond of the cyclopentadienyl vinylidene rhodium compound. The unsubstituted allene complex $(C_5H_5)Rh(\eta^2\text{-}CH_2{=}C{=}CH_2)(P\text{-}i\text{-}Pr_3)$ is accessible via the same route.[5,28] It is worth mentioning that in contrast to other allene transition-metal compounds,[29] both isomers of **12** are rigid at room temperature on the NMR time scale.

In agreement with the proposed mechanism for the reaction of **3** with HX (see Scheme II), protonation of **12** with HBF_4 in ether followed by metathesis of the immediately formed precipitate with NH_4PF_6 in methanol gives the 1-methylallyl complex *t,a*-**5c** (eq 1). If an equimolar amount of CF_3CO_2H is used and the reaction with **12** in CD_3NO_2 at 25 °C monitored by ^1H NMR, again only the formation of the cation of *t,a*-**5c** is observed. Even when the temperature is lowered, no intermediate such as the σ-methylallyl species **10** (see Scheme II) has been detected. From these results, it therefore cannot be conclusively decided if in the reaction of **12** with acids the attack of the proton is primarily directed to the metal or to the C^2 carbon of the methylallene unit.

Support for the assumption that at least for CF_3CO_2H the first possibility is much more likely comes from the following experiment. If the allene complex **12** in the presence of NaI is treated in acetone at −78 °C with trifluoroacetic acid in a 1:1 molar ratio, only the vinylrhodium compound **11** is produced (eq 1). We therefore suppose that **12** reacts with CF_3CO_2H to give the cationic species **9** that, according to Scheme II, is in equilibrium with both **8** and **10**, respectively. Under the conditions used for the experiment, the formation of the vinyl intermediate obviously is favored, and in the presence of iodide it is trapped to form **11**.

Conclusion

The present study has confirmed that the but-2-yne rhodium complex $(C_5H_5)Rh(MeC{\equiv}CMe)(P\text{-}i\text{-}Pr_3)$ (**3**) smoothly reacts with Brønsted acids and therefore behaves similarly to various other members of the $(C_5H_5)Rh(L)(PR_3)$ family. The final product of the protonation reaction is the (1-methylallyl)rhodium cation $[(C_5H_5)Rh(C_4H_7)(P\text{-}i\text{-}Pr_3)]^+$ that contains the 1-substituted allyl group in either the anti or the (thermodynamically preferred) syn configuration and in the anti conformation with regard to the phosphine ligand. The conversion of the alkyne into the 1-methylallyl unit occurs via several intermediates of which the vinylrhodium cation **8** (see Scheme II) can be trapped in presence of iodide to form the iodo derivative $[(C_5H_5)Rh((E)\text{-}CH_3C{=}CHCH_3)(P\text{-}i\text{-}Pr_3)I]$ (**11**). In absence of I^-, **8** rearranges to give the isomeric cation $[(C_5H_5)RhH(\eta^2\text{-}CH_2{=}CH{=}CHCH_3)(P\text{-}i\text{-}Pr_3)]^+$ (**9**) that on deprotonation by NH_3 produces the neutral allene complex **12**. The fact that an allene ligand is indeed formed during the conversion of but-2-yne into the allyl group $1\text{-}CH_3CHCHCH_2$ has also been confirmed by deuteriation experiments.

It should finally be noted that the one-step synthesis of **11** starting from either **3** or **12** and CF_3CO_2H/NaI also represents a new route to η^1-alkenyl transition-metal compounds. Recent work from various laboratories has shown that those compounds are generally obtained by *nucleophilic* attack on neutral or, in particular, *cationic* alkyne metal complexes,[24,30,31] and that they can be used to selectively prepare highly functionalized alkenes in good yield.[32]

The reaction of alkyne complexes, such as $(C_5H_5)Rh(RC{\equiv}CR')(P\text{-}i\text{-}Pr_3)$ in which the groups R and R′ can be varied over a wide range,[27a] with *electrophiles* in presence of a coordinating anion could be an alternative method to achieve this goal. The conversion of the vinyl compound **11** with $LiAlH_4$ to give the olefin complex **6** already indicates that on stepwise addition of an electrophilic and a nucleophilic reagent to the C≡C triple bond of alkynes substituted alkenes can be obtained. The question of whether the olefinic ligand (e.g., in **6**) can be displaced by an alkyne, thus re-forming the starting material $(C_5H_5)Rh(RC{\equiv}CR')(P\text{-}i\text{-}Pr_3)$, is currently being investigated in our laboratory.

Experimental Section

All operations were carried out under either purified nitrogen or argon. The starting material $[RhCl(C_8H_{14})_2]_2$ was prepared by a published procedure.[33]

Preparation of *trans*-$[RhCl(C_2Me_2)(P\text{-}i\text{-}Pr_3)_2]$ (2). A suspension of $[RhCl(C_8H_{14})_2]_2$ (500 mg, 0.70 mmol) in 50 mL of pentane was treated with P-*i*-Pr_3 (1.0 mL, 5.0 mmol) and stirred for 15 min at room temperature. The solution was filtered, the filtrate was cooled to 0 °C, and C_2Me_2 (81 mg, 1.50 mmol) was added. After 5 min the solvent and other volatile substances were

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removed in vacuo and the residue was dried and recrystallized from pentane (+25 to −78 °C). Orange, air-sensitive crystals were obtained: yield 450 mg (63%); mp 103 °C dec; ^{1}H NMR (C_6H_6) δ 2.52 (m, PCH), 2.24 (d, J(RhH) = 1.3 Hz, C_2Me_2), 1.54 (dvt, N = 12.4 Hz, J(HH) = 6.2 Hz, PCHCH_3). Anal. Calcd for $C_{22}H_{48}ClP_2Rh$: C, 51.68; H, 9.96; Rh, 19.81. Found: C, 51.52; H, 9.43; Rh, 20.06.

Preparation of (C_5H_5)Rh(C_2Me_2)(P-*i*-Pr_3) (3). A solution of **2** (250 mg, 0.49 mmol) in 20 mL of THF was treated with NaC_5H_5 (90 mg, 1.02 mmol) and stirred for 2 h at room temperature. The solvent was removed in vacuo and the residue extracted with hexane. The hexane solution was filtered, the filtrate was brought to dryness, and the dark oily residue was kept in vacuo for 6 h. The residue was then dissolved in 1 mL of THF and the solution treated with 10 mL of methanol and slowly cooled to −78 °C. After the solution was left standing for 3 h, yellow air-sensitive crystals were formed which were filtered, washed with cold methanol, and recrystallized from pentane (+25 to −78 °C): yield 118 mg (63%); mp 158 °C dec; MS (70 eV), m/e (I_r) 382 (17, M^+), 328 (100, $M^+ - C_2Me_2$), 168 (25, $C_5H_5Rh^+$); IR (KBr) ν(C≡C) 1910 cm^{-1}; ^{1}H NMR (C_6H_6) δ 5.49 (dd, J(PH) = 1.4 Hz, J(RhH) = 0.7 Hz, C_5H_5), 2.47 (dd, J(RhH) = 1.3 Hz, J(PH) = 0.3 Hz, C_2Me_2), 1.86 (m, PCH), 1.27 (dd, J(PH) = 12.8 Hz, J(HH) = 7.2 Hz, PCHCH_3). Anal. Calcd for $C_{18}H_{32}PRh$: C, 56.55; H, 8.44; Rh, 26.91. Found: C, 56.60; H, 8.63; Rh, 27.12.

Preparation of (C_5H_5)RhCH_3(P-*i*-Pr_3)I (4). A solution of **3** (210 mg, 0.55 mmol) in 10 mL of CH_3NO_2 was treated with an excess of methyl iodide (ca. 0.3 mL) and stirred for 45 min at room temperature. The solvent was removed in vacuo and the residue extracted with ether. The ether solution was concentrated in vacuo to ca. 2 mL, and 10 mL pentane was added. After the solution was cooled to −78 °C, red-brown, air-stable crystals were formed which were filtered, washed with cold pentane, and dried in vacuo: yield 211 mg (82%); mp 137 °C; MS (70 eV), m/e (I_r) 470 (1, M^+), 455 (4, $M^+ - CH_3$), 328 (13, $M^+ - CH_3I$), 168 (6, $C_5H_5Rh^+$). Anal. Calcd for $C_{15}H_{29}IPRh$: C, 38.32; H, 6.22; Rh, 21.89. Found: C, 38.35; H, 6.41; Rh, 21.77.

Preparation of [(C_5H_5)Rh(η^3-1-MeC_3H_4)(P-*i*-Pr_3)]PF_6 (Transoid,Anti Isomer) (*t*,*a*-5c). (a) A solution of **3** (135 mg, 0.35 mmol) in 5 mL of ether was treated with CF_3CO_2H (42 mg, 0.37 mmol) and stirred for 45 min at room temperature. A yellow precipitate was formed which was filtered off, repeatedly washed with ether, dried in vacuo, and dissolved in 3 mL of methanol which was saturated with NH_4PF_6. After the solution was stirred for 15 min, the yellow solid was filtered off, washed with methanol (2 × 3 mL) and ether, and recrystallized from nitromethane/ether; yield 142 mg (76%). (b) A solution of **3** (231 mg, 0.60 mmol) in 10 mL of ether was treated dropwise with a 50% solution of HBF_4 in ether until no further precipitate was formed. The yellow solid was filtered off and worked up as described above (see (a)); yield 262 mg (82%). (c) A solution of **3** (84 mg, 0.22 mmol) in 2 mL of nitromethane was treated with NH_4PF_6 (160 mg, 0.98 mmol) and stirred for 45 min at room temperature. The solvent was removed in vacuo, and the solid residue was washed with small amounts of methanol and recrystallized from nitromethane/ether: yield 53 mg (46%); equivalent conductivity (CH_3NO_2) Λ = 94 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{18}H_{33}F_6P_2Rh$: C, 40.92; H, 6.30; Rh, 19.48. Found: C, 40.85; H, 6.45; Rh, 19.70.

Preparation of [(C_5H_5)Rh(η^3-1-MeC_3H_4)(P-*i*-Pr_3)]PF_6 (Transoid,Syn Isomer) (*t*,*s*-5c). A solution of *t*,*a*-**5c** (87 mg, 0.16 mmol) in 5 mL of nitromethane was stirred for 3 h at 60 °C. The solution was concentrated in vacuo to ca. 2 mL, and 10 mL of ether was added. A yellow precipitate was formed which was filtered off, repeatedly washed with ether, and dried in vacuo: yield 80 mg (92%); equivalent conductivity (CH_3NO_2) Λ = 110 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{18}H_{33}F_6P_2Rh$: C, 40.92; H, 6.30; Rh, 19.48. Found: C, 40.87; H, 5.98; Rh, 19.60.

Preparation of (C_5H_5)Rh((*Z*)-CHMe=CHMe)(P-*i*-Pr_3) (6). A solution of *t*,*a*-**5c** (137 mg, 0.26 mmol) in 10 mL of THF was treated at −78 °C with $LiAlH_4$ (10 mg, 0.26 mmol) and with continuous stirring slowly warmed to room temperature. After removal of the solvent in vacuo, the residue was extracted with pentane (2 × 5 mL). The pentane solution was filtered, concentrated to ca. 2 mL, and cooled to −78 °C. Yellow, air-sensitive crystals were formed which were filtered off, washed with cold (−78 °C) pentane (2 × 1 mL), and dried in vacuo: yield 89 mg (89%); mp 78–80 °C; MS (70 eV), m/e (I_r) 384 (6, M^+), 328 (100, $M^+ - C_2H_2Me_2$), 168 (27, $C_5H_5Rh^+$), 56 (11, $C_2H_2Me_2^+$); ^{1}H NMR (C_6H_6) δ 5.08 (dd, J(PH) = 1.1 Hz, J(RhH) = 0.7 Hz, C_5H_5), 2.28 (m, $C_2H_2(CH_3)_2$), 1.78 (d, J(HH) = 5.4 Hz, $C_2H_2(CH_3)_2$), 1.65 (m, PCH), 1.00 (dd, J(PH) = 12.5 Hz, J(HH) = 6.4 Hz, PCHCH_3). Anal. Calcd for $C_{18}H_{34}PRh$: C, 56.25; H, 8.92; Rh, 26.77. Found: C, 56.05; H, 8.95; Rh, 26.65.

Preparation of (C_5H_5)Rh((*E*)-CCH_3=$CHCH_3$)(P-*i*-Pr_3)I (11). A suspension of **3** (230 mg, 0.60 mmol) and NaI (180 mg, 1.20 mmol) in 10 mL of THF was treated with CF_3CO_2H (89 mg, 0.60 mmol) at room temperature. After the solution was stirred for 10 min, the solvent was removed, the residue was extracted with ether (2 × 5 mL), and the ether solution was brought to dryness. Recrystallization from toluene/pentane (1:20) at −78 °C gave red-brown, air-sensitive crystals: yield 255 mg (83%); mp 86–87 °C dec; MS (70 eV), m/e (I_r) 510 (1, M^+), 382 (2, M^+ − HI), 328 (10, C_5H_5(P-*i*-Pr_3)Rh^+), 295 (1, $C_5H_5RhI^+$), 168 (5, $C_5H_5Rh^+$); ^{1}H NMR (C_6D_6) δ 5.60 (m, CHCH$_3$), 5.17 (dd, J(PH) = 1.8 Hz, J(RhH) = 0.5 Hz, C_5H_5), 2.61 (m, PCH), 2.57 (s, CCH_3), 1.77 (d, J(HH) = 6.4 Hz, CHCH_3), 1.14 (dd, J(PH) = 13.9 Hz, J(HH) = 7.1 Hz, PCHCH_3), 0.97 (dd, J(PH) = 12.7 Hz, J(HH) = 7.1 Hz, PCHCH_3). Anal. Calcd for $C_{18}H_{33}IPRh$: C, 42.37; H, 6.52; Rh, 20.17. Found: C, 42.83; H, 6.50; Rh, 20.00.

Reaction of 11 with $LiAlH_4$. A solution of **11** (78 mg, 0.15 mmol) in 10 mL of ether was treated at −78 °C with $LiAlH_4$ (6 mg, 0.16 mmol) and under continuous stirring slowly warmed to room temperature. The solvent was removed in vacuo, the residue was extracted with pentane (2 × 3 mL), and the pentane solution was brought to dryness. The remaining yellow oil according to the ^{1}H NMR spectrum consists of **6** (ca. 85%) and (C_5H_5)-RhH_2(P-*i*-Pr_3) (ca. 15%).

Preparation of (C_5H_5)Rh(η^2-(*E*)-CH_2=C=$CHCH_3$)(P-*i*-Pr_3) (12). (a) A solution of **3** (240 mg, 0.63 mmol) in 2 mL of hexane was chromatographed on Al_2O_3 (Woelm, neutral, activity grade V) by using a 20 cm long column with hexane. The yellow eluate was brought to dryness in vacuo, and the oily residue was dissolved in 5 mL of acetone. After the solution was left standing at −20 °C for 3 days, yellow, air-sensitive crystals were formed that were filtered off, washed with cold acetone, and dried in vacuo: yield 202 mg (84%); mp 48 °C. (b) A solution of **3** (164 mg, 0.43 mmol) in 5 mL of nitromethane was treated with NH_4PF_6 (260 mg, 1.59 mmol) and stirred for 4 min at room temperature. The solvent was removed in vacuo, the residue was extracted with pentane (3 × 3 mL), and the pentane solution was brought to dryness. The oily residue according to the ^{1}H NMR spectrum consists of **12**: yield 24 mg (15%); MS (70 eV), m/e (I_r) 382 (17, M^+), 328 (100, $M^+ - C_4H_6$), 168 (40, $C_5H_5Rh^+$), 54 (15, $C_4H_6^+$); ^{1}H NMR (C_6D_6) δ 5.49 (m, CHCH$_3$), 5.08 (dd, J(PH) = 1.2 Hz, J(RhH) = 0.6 Hz, C_5H_5), 2.29 (m, 1 H of =CH_2; the signal of the other CH_2 proton is probably obscured by the signals of the phosphine protons), 2.06 (ddd, ^3J(HH) = 6.3 Hz, ^5J(HH) = 1.6 Hz, ^5J(HH) = 1.6 Hz, CHCH_3), 1.48 (m, PCH), 1.03 (dd, J(PH) = 12.9 Hz, J(HH) = 6.8 Hz, PCHCH_3; the two signals for the diastereotopic methyl groups not separated due to very small difference in chemical shift); ^{13}C NMR (C_6D_6) δ 156.80 (dd, J(RhC) = 23.5 Hz, J(PC) = 6.6 Hz, =C=), 110.36 (s, $CHCH_3$), 86.64 (dd, J(RhC) = J(PC) = 2.9 Hz, C_5H_5), 25.73 (d, J(PC)= 20.6 Hz, PCH), 22.03 (s, CHCH_3), 20.04 (s, PCHCH_3), 19.95 (s, PCHCH_3), −1.95 (dd, J(RhC) = 12.5 Hz, J(PC) = 2.2 Hz, =CH_2). Anal. Calcd for $C_{18}H_{32}PRh$: C, 56.55; H, 8.44; Rh, 26.91. Found: C, 56.55; H, 8.49; Rh, 27.24.

If the solution of **3** was chromatographed on Al_2O_3 which was deactivated with D_2O and the eluate worked up as described above, a yellow oil of **12**-d_1 was obtained; yield quantitatively; MS (70 eV), m/e (I_r) 383 (20, M^+), 328 (100, $M^+ - C_4H_5D$). The ^{1}H NMR spectrum was almost identical with that of **12** without showing the signal at δ 5.49 for the allenic proton.

Preparation of 11 from 12. A solution of **12** (184 mg, 0.48 mmol) and NaI (150 mg, 1.00 mmol) in 10 mL of acetone was treated at −78 °C with CF_3CO_2H (56 mg, 0.49 mmol). Under continuous stirring, the solution was slowly warmed to room temperature and worked up as described above; yield (of **11**) 146 mg (59%).

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Stepwise Synthesis of Heteronuclear Pt_2M and PdPtM Clusters (M = Cr, Mo, W)

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The dinuclear complex $(\mu\text{-}C_5H_5)(\mu\text{-}2\text{-}MeC_3H_4)Pt_2(P\text{-}i\text{-}Pr_3)_2$ (**1**), which is prepared from $(\eta^5\text{-}C_5H_5)Pt(\eta^3\text{-}2\text{-}MeC_3H_4)$ and $Pt(P\text{-}i\text{-}Pr_3)_2$, reacts with Me_3SiBr to produce the structurally related compound $(\mu\text{-}2\text{-}MeC_3H_4)(\mu\text{-}Br)Pt_2(P\text{-}i\text{-}Pr_3)_2$ (**4**). Reaction of **4** with $[(C_5H_5)M(CO)_3]Na$ (M = Mo, W) leads to displacement of the bridging bromide by the tricarbonyl(cyclopentadienyl)metal anion and formation of the trinuclear clusters $(C_5H_5)(2\text{-}MeC_3H_4)(CO)_3(P\text{-}i\text{-}Pr_3)_2Pt_2M$ (**5**, **6**). The analogous mixed-metal PdPtM complexes **9**–**11** are similarly prepared, starting from $(\mu\text{-}C_5H_5)(\mu\text{-}2\text{-}MeC_3H_4)PdPt(P\text{-}i\text{-}Pr_3)_2$ (**7**) via $(\mu\text{-}2\text{-}MeC_3H_4)(\mu\text{-}Br)PdPt(P\text{-}i\text{-}Pr_3)_2$ (**8**) as the intermediate that subsequently reacts with $[(C_5H_5)M(CO)_3]Na$ (M = Cr, Mo, W) to form $(C_5H_5)(2\text{-}MeC_3H_4)(CO)_3(P\text{-}i\text{-}Pr_3)_2PdPtM$ (**9**–**11**). The IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopic data of **5**, **6**, and **9**–**11** confirm that the new heteronuclear clusters contain a tetrahedral Pt_2MC or PdPtMC framework, the carbon atom of which belongs to a triply bridging CO group.

Introduction

The chemistry of mixed-metal clusters is currently of high interest because of the unique reactivity patterns that are to be expected as a consequence of adjacent metals with different types of chemical properties.[1] Although some rational synthetic methods have recently become available,[2,3] it still remains difficult to predict the exact composition of a heteronuclear metal–metal bonded product that could result from a given reaction. Therefore it is still a challenge to develop routes that produce cluster-type compounds in a *stepwise* fashion, providing *high yields* and avoiding the formation of side products with similar properties.

During the last 10 years we have shown that various dinuclear palladium and platinum complexes of general formula $(\mu\text{-}X)(\mu\text{-}Y)M_2(PR_3)_2$ (M = Pd, Pt) can be prepared by a route which we designated as "1 + 1 addition", that is by combination of two mononuclear starting materials, $M(PR_3)_2$ and $(X)M(Y)$.[4] Particularly for M = Pd, the bridging ligands X and Y can easily be displaced *without cleavage* of the M–M bond. Owing to this robust nature we tried to introduce not only "classical" bridging ligands such as chloride or acetate but also organometallic anions in the hope that this would provide a new entry into the field of mixed-metal clusters. We were highly encouraged by MO calculations from Hofmann,[5] which led to the prediction that carbonyl metal complexes such as $[Co(CO)_4]^-$ or $[(C_5H_5)Mo(CO)_3]^-$ should be useful reagents for the desired purpose.

The first experiments using dinuclear palladium compounds $(\mu\text{-}C_5H_5)(\mu\text{-}X)Pd_2(PR_3)_2$ and $(\mu\text{-}2\text{-}MeC_3H_4)(\mu\text{-}X)Pd_2(PR_3)_2$ (X = Cl, Br, CH_3CO_2) as starting materials have confirmed the prediction.[6,7] In this paper we describe an extension of our original work which proves that also complexes containing Pt–Pt and Pd–Pt bonds can be employed as precursors for the synthesis of new heteronuclear clusters. A short communication reporting some preliminary results has already appeared.[8]

Results and Discussion

The dinuclear complex $(\mu\text{-}C_5H_5)(\mu\text{-}2\text{-}MeC_3H_4)Pt_2(P\text{-}i\text{-}Pr_3)_2$ (**1**), which is prepared from $(\eta^5\text{-}C_5H_5)Pt(\eta^3\text{-}2\text{-}MeC_3H_4)$ and $Pt(P\text{-}i\text{-}Pr_3)_2$,[9] reacts with $[(C_5H_5)Mo(CO)_3]Na$ not to produce a Pt_2Mo cluster but to give the mononuclear compound $(\eta^1\text{-}C_5H_5)Pt(\eta^3\text{-}2\text{-}MeC_3H_4)(P\text{-}i\text{-}Pr_3)$ (**2**).[10] The attempt to displace the cyclopentadienyl bridge in **1** by acetate, which should provide a more reactive starting material, also failed because in the reaction of **1** with acetic acid (see Scheme I) only the formation of complex **3** was observed.

The five-membered-ring ligand in **1** can be displaced, however, by bromide with Me_3SiBr as a reagent. By this

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