Synthesis and Properties of Cationic Hydrido(tertiary phosphine)ruthenium(II) Complexes

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The cationic complex *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ can be synthesized from *cis*-$RuH_2(PMe_3)_4$ and 1 equiv of NH_4PF_6 in Et_2O. An excess of NH_4PF_6 leads to the formation of the dicationic species *cis*-$[Ru(NH_3)_2(PMe_3)_4][PF_6]_2$. The NH_3 ligand in *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ can be readily replaced by an appropriate ligand to give monohydrido complexes of the type *cis*-$[RuH(L)(PMe_3)_4]PF_6$ (L = CH_3CN, CO, PMe_3). Whereas the substitution of the NH_3 ligand with ethene or tolane was not possible, the reaction of *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ with a terminal alkyne such as phenylacetylene leads to the formation of styrene and *cis*-$[Ru(C{\equiv}CPh)(NH_3)(PMe_3)_4]PF_6$. The neutral dihydrido complex *cis*-$RuH_2(PMe_3)_4$ reacts with terminal alkynes HC≡CR to give bis(alkynyl) complexes *trans*-$Ru(C{\equiv}Cr)_2(PMe_3)_4$ (R = Ph, $SiMe_3$, CO_2Me). An NMR study of the reaction indicated involvement of intermediates *cis*-$RuH(C{\equiv}CR)(PMe_3)_4$ and *cis*-$Ru(C{\equiv}CR)_2(PMe_3)_4$. The cationic complexes *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ and *cis*-$[Ru(C{\equiv}CPh)(NH_3)(PMe_3)_4]PF_6$ catalyze dimerization of the alkyne to give mainly (*Z*)-1,4-diphenylbuten-3-yne.

Introduction

In contrast to neutral organotransition metal complexes the chemistry of cationic metal complexes has attracted less attention until recently. Concerning early transition metal complexes, the importance of the role of cationic alkylzirconium or titanium complexes such as Cp_2ZrR^+ and Cp_2TiR^+ in polymerization of olefin monomers has been recognized.[1] In the course of our studies of the organometallic chemistry of late transition metals our attention has been drawn to the difference in behavior between the neutral and cationic organopalladium complexes. Removal of the halide ligand from mono-alkyl palladium halide complexes caused remarkable enhancement in the reactivities of neutral organopalladium complexes. The ethylpalladium complexes become very susceptible to β-hydrogen elimination on their conversion into the cationic complex[2a] and reactivities of arylpalladium complexes to olefin and CO insertion are markedly enhanced by converting them into cationic complexes.[2b-d] The reactivity enhancement effect by generation of a cationic organopalladium complex is considered to be related to the reactivity enhancement by addition of silver salts to the catalytic systems of Heck processes[2e-i] in arylation of olefins and carbonylation of aromatic halides.

Here we report the results of converting the neutral complex *cis*-$RuH_2(PMe_3)_4$ into cationic complex *cis*-$[RuH(L)(PMe_3)_4]PF_6$ in their reactivities toward alkynes and olefins. Particularly we focused our attention on the reactions of alkynes with the ruthenium complexes because of the importance of the catalytic processes to convert acetylenes into their dimers and polymers[3-5] as well as of metal-containing polymers with alkynyl-metal backbones.[6-8]

Results

Synthesis of Cationic Hydridoruthenium(II) Complexes from *cis*-$RuH_2(PMe_3)_4$. The parent PMe_3-

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coordinated neutral complex *cis*-$RuH_2(PMe_3)_4$ (**1**) can be prepared in several ways,[9] among which the route using *trans*-$RuCl_2(PMe_3)_4$[10] treated with sodium tetrahydroborate seems to be the most convenient.[11] Several ruthenium hydrido and/or dihydrogen complexes containing phosphine ligands have been reported,[4,5,12-15] but cationic hydrido complexes derived from *cis*-$RuH_2(PMe_3)_4$ (**1**) are almost unknown[13,14] and are therefore described in the following.

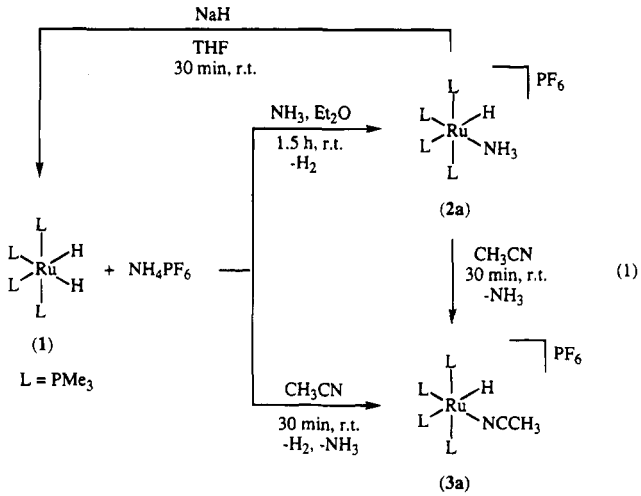
When a suspension of *cis*-$RuH_2(PMe_3)_4$ (**1**) and NH_4PF_6 (or NH_4BPh_4) in Et_2O is stirred at room temperature for 90 min under NH_3 atmosphere, *cis*-$[RuH(NH_3)(PMe_3)_4]X$ (X = PF_6 (**2a**), BPh_4 (**2b**)) are obtained in almost quantitative yields.

Compound **2a** is a colorless air-sensitive solid, which is readily soluble in polar organic solvents such as acetone, MeOH and THF. In solution, however, slow decomposition and formation of $[RuH(PMe_3)_5]PF_6$ [13] can be observed.

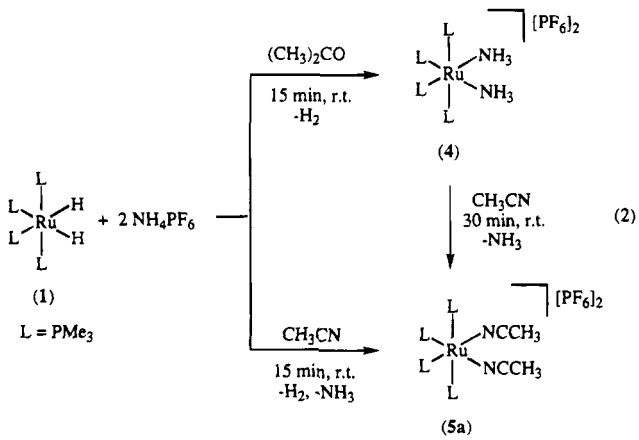
The characterization of **2a** was accomplished by elemental analysis and by means of ^1H, ^{31}P and ^{13}C NMR spectroscopy. In the IR spectrum of **2a** (KBr), there are two absorptions at 3408 (NH stretch mode) and 1628 cm^{-1} (NH deformation mode), and one intensive absorption at 1848 cm^{-1}, due to the Ru-H bond. The ^1H NMR spectrum shows a high-field signal (Ru-H) at −9.33 ppm as a doublet of triplets of doublets with P-H coupling constants of 91.5, 30.3 and 21.0 Hz. Furthermore the ^1H NMR spectrum has a singlet at 2.82 ppm (for NH_3). For the PMe_3 ligands a triplet at 1.51 ppm (J = 2.9 Hz, virtual coupling) and two doublets at 1.44 (J = 7.8 Hz) and at 1.42 ppm (J = 5.9 Hz) can be observed. The ^{31}P NMR spectrum consists of three well-resolved multiplets (A_2BC pattern: $\delta A = -4.10$, $\delta B = 15.20$, $\delta C = -14.33$; $J_{AB} = 36.7$, $J_{AC} = 22.7$, $J_{BC} = 24.2$ Hz), typical for a *cis*-$RuL'L''(PMe_3)_4$ complex.[14,15] In the ^{13}C NMR no other signals than the PMe_3 ligands could be found. The IR and NMR spectroscopic data of **2b** are similar and are summarized in Tables 1–3.

When complex **2a** is treated with CH_3CN and when the reaction of *cis*-$RuH_2(PMe_3)_4$ (**1**) with NH_4PF_6 (or NH_4BPh_4) is carried out in CH_3CN instead of Et_2O, the acetonitrile-coordinated hydridoruthenium complexes *cis*-$[RuH(NCCH_3)(PMe_3)_4]X$ (X = PF_6 **3a**, BPh_4 **3b**), are obtained in almost quantitative yields.

With hydride-donating reagents, such as NaH, *cis*-$[RuH(NH_3)(PMe_3)_4]$-PF_6 (**2a**) can be converted back into the known dihydride complex **1**. Treatment of complex **2a** with $NaBH_4$ leads to the formation of $RuH(\eta^2\text{-}BH_4)(PMe_3)_3$, which reacts with added PMe_3 to give complex **1**.



On treatment of *cis*-$RuH_2(PMe_3)_4$ (**1**) with 2 equiv of NH_4PF_6 in acetone or CH_3CN the dicationic complexes *cis*-$[Ru(NH_3)_2(PMe_3)_4][PF_6]_2$ (**4**) and *cis*-$[Ru(NCCH_3)_2(PMe_3)_4][PF_6]_2$ (**5a**), respectively, are formed. It should be mentioned that also a conversion of complex **4** into **5a** is possible in the presence of CH_3CN. Treatment of **1** with 2 equiv of HBF_4 in CH_3CN leads to the formation of *cis*-$[Ru(NCCH_3)_2(PMe_3)_4][BF_4]_2$ (**5b**). Related, dicationic iron complexes with organonitriles as ligands *trans*-$[Fe(NCR)_2(depe)_2]^{2+}$ have been reported.[16]



The complexes **4** and **5a,b** are colorless air-stable solids, which are easily soluble in polar organic solvents such as acetone, MeOH and THF. All complexes could

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Table 1. ^{1}H NMR Spectroscopic Data[a]

compound	δ, ppm	mult[a]	J, Hz	assignment
2a,[b] *cis*-[RuH(NH_3)(PMe_3)$_4$]PF_6	2.82	s		NH_3
	1.51	t	2.9	*trans*-PMe_3
	1.44	d	7.8	*cis*-PMe_3
	1.42	d	5.9	*cis*-PMe_3
	−9.33	dtd	91.5, 30.3, 21.0	RuH
2b,[b] *cis*-[RuH(NH_3)(PMe_3)$_4$]BPh_4	6.74−7.41	m		BPh_4
	2.80	s		NH_3
	1.50	t	2.6	*trans*-PMe_3
	1.43	d	7.3	*cis*-PMe_3
	1.40	d	5.5	*cis*-PMe_3
	−9.36	dtd	90.9, 30.2, 20.9	RuH
3a,[b] *cis*-[RuH($NCCH_3$)(PMe_3)$_4$]PF_6	2.46	s		CH_3CN
	1.51	t	2.9	*trans*-PMe_3
	1.43	d	7.7	*cis*-PMe_3
	1.42	d	6.2	*cis*-PMe_3
	−9.32	dq	89.5, 24.6	RuH
3b,[b] *cis*-[RuH($NCCH_3$)(PMe_3)$_4$]BPh_4	6.74−7.33	m		BPh_4
	2.39	s		CH_3CN
	1.51	t	3.0	*trans*-PMe_3
	1.42	d	8.0	*cis*-PMe_3
	1.41	d	5.9	*cis*-PMe_3
	−9.31	dq	89.5, 24.6	RuH
4,[b] *cis*-[Ru(NH_3)$_2$(PMe_3)$_4$][PF_6]$_2$	2.80	d	8.8	NH_3
	1.69	t	2.9	*trans*-PMe_3
	1.64	t	4.0	*cis*-PMe_3
5a,[b] *cis*-[Ru($NCCH_3$)$_2$(PMe_3)$_4$][PF_6]$_2$	2.66	s		CH_3CN
	1.73	t	3.3	*trans*-PMe_3
	1.64	t	4.4	*cis*-PMe_3
5b,[b] *cis*-[Ru($NCCH_3$)$_2$(PMe_3)$_4$][BF_4]$_2$	2.64	s		CH_3CN
	1.71	t	3.3	*trans*-PMe_3
	1.63	t	4.4	*cis*-PMe_3
6,[b] *cis*-[RuH(CO)(PMe_3)$_4$]PF_6	1.66	t	2.9	*trans*-PMe_3
	1.62	d	7.7	*cis*-PMe_3
	1.59	d	6.6	*cis*-PMe_3
	−9.16	dq	74.5, 25.3	RuH
7,[b] *cis*-[Ru(C≡CPh)(NH_3)(PMe_3)$_4$]PF_6	7.04−7.26	m		Ph
	2.28	s		NH_3
	1.65	t	2.9	*trans*-PMe_3
	1.57	d	8.3	*cis*-PMe_3
	1.53	d	6.8	*cis*-PMe_3
8,[b] *cis*-[Ru(C≡CPh)(CO)(PMe_3)$_4$]PF_6	7.14−7.29	m		Ph
	1.81	t	3.5	*trans*-PMe_3
	1.71	d	7.3	*cis*-PMe_3
	1.70	d	7.7	*cis*-PMe_3
9,[c] *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$	6.91−7.10	m		Ph
	1.55	s br		PMe_3
10[c] *trans*-Ru(C≡C$SiMe_3$)$_2$(PMe_3)$_4$	1.55	s br		PMe_3
	0.00	s		$SiMe_3$
11,[d] *trans*-Ru(C≡CCO_2Me)$_2$(PMe_3)$_4$	3.56	s		CO_2Me
	1.50	s br		PMe_3
12,[b] *cis*-RuH(C≡CPh)(PMe_3)$_4$	7.25−7.52	m		Ph
	1.51	t	2.6	*trans*-PMe_3
	1.36	d	5.9	*cis*-PMe_3
	1.31	d	5.9	*cis*-PMe_3
	−9.71	dq	86.6, 26.4	RuH
13,[b] *cis*-Ru(C≡CPh)$_2$(PMe_3)$_4$	7.32−7.51	m		Ph
	1.62	t	2.9	*trans*-PMe_3
	1.44	t	3.7	*cis*-PMe_3

[a] The multiplicities d and t, when applied to the PMe_3 resonances, refer to apparent splitting patterns. Accordingly, the values reported as coupling constants for these resonances are the separation between the lines and do not necessarily reflect the true coupling constants. [b] $(CD_3)_2CO$. [c] CD_2Cl_2. [d] $CDCl_3$.

be characterized by elemental analysis and by means of ^{1}H, ^{31}P and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra of **4**, **5a**, and **5b** show two triplets at 1.69 (t, J = 2.9 Hz) and at 1.64 ppm (t, J = 4.0 Hz) for **4**, at 1.73 (t, J = 3.3 Hz) and at 1.64 ppm (t, J = 4.4 Hz) for **5a**, and at 1.71 (t, J = 3.3 Hz) and at 1.63 ppm (t, J = 4.4 Hz) for **5b**, respectively, whereas no hydride signal was observed. The ^{31}P NMR spectra show an A_2B_2-spin system: **4**: δA = 6.53, δB = −7.87 ppm; J_{AB} = 31.6 Hz; **5a**: δA = 8.55, δB = −7.35 ppm; J_{AB} = 32.3 Hz; **5b**: δA = 8.57, δB = −7.27 ppm; J_{AB} = 31.5 Hz. The coupling pattern of the PMe_3 ligands is consistent with the cis-structure of the complexes.[14,15]

In order to learn more about the properties of these metallorganic species, the most reactive species, complex **2a**, was treated with CH_3CN (see eq 1), CO (see eq 3) and PMe_3. In all cases the reactions give the corresponding substitution products *cis*-[RuH(L)(PMe_3)$_4$]-PF_6 (L = CH_3CN (**3a**), CO (**6**), PMe_3 [13]) in a few minutes. The hydridoruthenium compounds **3a** and **6** were obtained as colorless, moderately air- stable solids, which are easily soluble in polar organic solvents, and were characterized by IR, NMR and elemental analysis.

Reactions of the Cationic Hydridoruthenium Complexes with Alkynes. Although the NH_3 ligand in **2a** did not undergo the exchange with $H_2C{=}CH_2$ and

Table 2. $^{13}C\{^1H\}$ NMR Spectroscopic Data[a]

compound	δ, ppm	mult[a]	*J*, Hz	assignment
2a,[b] *cis*-[RuH(NH_3)(PMe_3)$_4$]PF_6	26.78	dq	30.1, 3.4	*cis*-PMe_3
	22.73	td	18.5, 1.0	*trans*-PMe_3
	21.77	dt	13.9, 3.4	*cis*-PMe_3
2b,[b] *cis*-[RuH(NH_3)(PMe_3)$_4$]BPh_4	164.49	m		PBh_4
	136.96	s		
	125.85	m		
	122.09	s		
	26.19	dq	29.7, 3.9	*cis*-PMe_3
	22.89	td	13.8, 3.4	*trans*-PMe_3
	21.94	dt	18.2, 2.2	*cis*-PMe_3
3a,[b] *cis*-[RuH($NCCH_3$)(PMe_3)$_4$]PF_6	125.30	dbr	15.0	CH_3CN
	22.12	m		PMe_3
	22.95	m		PMe_3
	21.41	m		PMe_3
	3.15	sbr		CH_3CN
3b,[b] *cis*-[RuH($NCCH_3$)(PMe_3)$_4$]BPh_4	164.53	m		BPh_4
	136.93	s		
	125.87	m		
	122.12	s		
	128.50	tbr	9.0	CH_3CN
	25.29	dq	30.0, 3.9	*cis*-PMe_3
	23.16	td	14.3, 3.1	*trans*-PMe_3
	21.59	dt	19.6, 2.2	*cis*-PMe_3
	3.28	sbr		CH_3CN
5a,[b] *cis*-[Ru($NCCH_3$)$_2$(PMe_3)$_4$][PF_6]$_2$	127.83	sbr		CH_3CN
	20.93	m		PMe_3
	18.17	t	15.0	PMe_3
	3.62	sbr		CH_3CN
5b,[b] *cis*-[Ru($NCCH_3$)$_2$(PMe_3)$_4$][BF_4]$_2$	127.85	sbr		CH_3CN
	20.88	m		PMe_3
	18.10	t	14.8	PMe_3
	3.61	sbr		CH_3CN
6,[b] *cis*-[RuH(CO)(PMe_3)$_4$]PF_6	203.00	dtd	77.0, 14.4, 9.9	CO
	23.56	tdd	16.3, 3.0, 2.3	*trans*-PMe_3
	22.12	dq	28.3, 4.2	*cis*-PMe_3
	21.94	dq	24.1, 2.0	*cis*-PMe_3
7,[b] *cis*-[Ru(C≡CPh)(NH_3)(PMe_3)$_4$]PF_6	131.54	s		Ph
	130.75	s		
	129.35	s		
	125.74	s		
	109.95	d	22.1	Ru-*C*≡C[d]
	23.70	d	30.2	*cis*-PMe_3
	22.50	d	30.2	*cis*-PMe_3
	19.44	t	14.1	*trans*-PMe_3
8,[b] *cis*-[Ru(C≡CPh)(CO)(PMe_3)$_4$]PF_6	199.21	dtd	74.8, 14.9, 5.9	CO
	130.86	s		Ph
	129.35	s		
	128.87	s		
	125.74	s		
	110.21	d br	19.5	Ru-*C*≡C[d]
	22.28	ddt	27.0, 3.0, 2.0	*cis*-PMe_3
	20.07	td	16.5, 1.5	*trans*-PMe_3
	19.06	ddt	27.6, 4.2, 3.2	*cis*-PMe_3
9,[c] *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$	132.45	quin	15.7	Ru-*C*≡C
	131.62	quin	1.3	Ph
	130.29	quin	1.3	
	128.14	s		
	122.86	s		
	108.22	quin	1.2	Ru-C≡*C*
	20.22	s br		PMe_3
10,[c] *trans*-Ru(C≡CSiMe_3)$_2$(PMe_3)$_4$	157.45	quin	16.1	Ru-*C*≡C
	110.22	quin	1.0	Ru-C≡*C*
	19.60	s br		PMe_3
	1.84	t br	0.5	$SiMe_3$
11,[c] *trans*-Ru(C≡CCO_2Me)$_2$(PMe_3)$_4$	153.84	quin	1.4	*C*O_2Me
	145.93	quin	16.1	Ru-*C*≡C
	101.98	quin	1.8	Ru-C≡*C*
	51.25	s		CO_2*Me*
	19.56	quin	3.0	PMe_3

[a] The multiplicities d and t, when applied to the PMe_3 resonances, refer to apparent splitting patterns. Accordingly, the values reported as coupling constants for these resonances are the separation between the lines and do not necessarily reflect the true coupling constants. [b] $(CD_3)_2CO$. [c] CD_2Cl_2. [d] Signal of Ru-C≡*C* not observed.

PhC≡CPh, **2a** readily reacted with phenylacetylene in acetone at room temperature to give *cis*-[Ru(C≡CPh)(NH_3)(PMe_3)$_4$]PF_6 (**7**) with liberation of styrene.

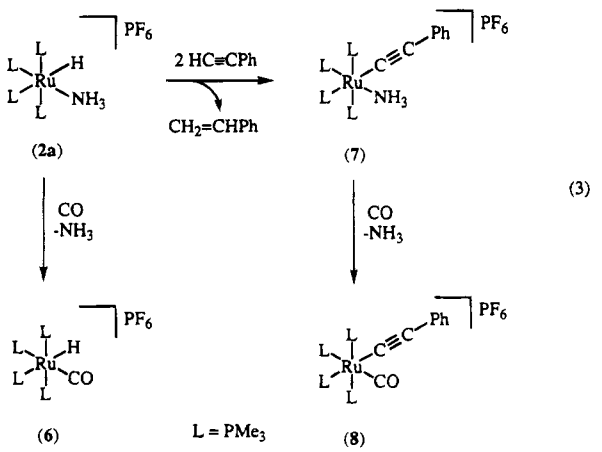
Complex **7** was obtained as a colorless, air-sensitive solid, which is easily soluble in polar organic solvents, and was characterized by IR and NMR (^1H, ^{13}C, ^{31}P) as

Table 3. $^{31}P\{^1H\}$ NMR Spectroscopic Data

compound	spin system	δ, ppm	J, Hz
2a,[a] *cis*-[RuH(NH_3)(PMe_3)$_4$]PF_6	A_2BC	$\delta A = -4.10$	$J_{AB} = 36.7$
		$\delta B = 15.20$	$J_{AC} = 22.7$
		$\delta C = -14.33$	$J_{BC} = 24.2$
2b,[a] *cis*-[RuH(NH_3)(PMe_3)$_4$]BPh_4	A_2BC	$\delta A = -3.55$	$J_{AB} = 36.7$
		$\delta B = 15.84$	$J_{AC} = 22.7$
		$\delta C = -13.71$	$J_{BC} = 23.5$
3a,[a] *cis*-[RuH($NCCH_3$)(PMe_3)$_4$]PF_6	A_2BC	$\delta A = -2.55$	$J_{AB} = 37.4$
		$\delta B = 15.20$	$J_{AC} = 22.7$
		$\delta C = -13.62$	$J_{BC} = 24.9$
3b,[a] *cis*-[RuH($NCCH_3$)(PMe_3)$_4$]BPh_4	A_2BC	$\delta A = -2.26$	$J_{AB} = 37.4$
		$\delta B = 15.46$	$J_{AC} = 22.8$
		$\delta C = -13.19$	$J_{BC} = 24.2$
4a,[a] *cis*-[Ru(NH_3)$_2$(PMe_3)$_4$][PF_6]$_2$	A_2B_2	$\delta A = 6.53$	$J_{AB} = 31.6$
		$\delta B = -7.87$	
5a,[a] *cis*-[Ru($NCCH_3$)$_2$(PMe_3)$_4$][PF_6]$_2$	A_2B_2	$\delta A = 8.55$	$J_{AB} = 32.3$
		$\delta B = -7.35$	
5b,[a] *cis*-[Ru($NCCH_3$)$_2$(PMe_3)$_4$][BF_4]$_2$	A_2B_2	$\delta A = 8.57$	$J_{AB} = 31.5$
		$\delta B = -7.27$	
6,[a] *cis*-[RuH(CO)(PMe_3)$_4$]PF_6	A_2BC	$\delta A = -8.97$	$J_{AB} = 22.0$
		$\delta B = -18.96$	$J_{AC} = 38.8$
		$\delta C = -12.85$	$J_{BC} = 36.7$
7,[a] *cis*-[Ru(C≡CPh)(NH_3)(PMe_3)$_4$]PF_6	A_2BC	$\delta A = -3.81$	$J_{AB} = 35.2$
		$\delta B = 13.87$	$J_{AC} = 27.1$
		$\delta C = -8.45$	$J_{BC} = 27.8$
8,[a] *cis*-[Ru(C≡CPh)(CO)(PMe_3)$_4$]PF_6	A_2BC	$\delta A = -10.21$	$J_{AB} = 24.9$
		$\delta B = -15.26$	$J_{AC} = 41.1$
		$\delta C = -14.62$	$J_{BC} = 36.6$
9,[b] *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$	A_4	−4.53	
10[b] *trans*-Ru(C≡CSiMe_3)$_2$(PMe_3)$_4$	A_4	−7.78	
11,[b] *trans*-Ru(C≡CCO_2Me)$_2$(PMe_3)$_4$	A_4	−9.93	
12,[a] *cis*-RuH(C≡CPh)(PMe_3)$_4$	A_2BC	$\delta A = -3.56$	$J_{AB} = 24.9$
		$\delta B = -14.61$	$J_{AC} = 31.5$
		$\delta C = -6.08$	$J_{BC} = 23.5$
13,[a] *cis*-Ru(C≡CPh)$_2$(PMe_3)$_4$	A_2B_2	$\delta A = -5.90$	$J_{AB} = 30.0$
		$\delta B = -9.56$	

[a] $(CD_3)_2CO$. [b] CD_2Cl_2.

well as by elemental analysis. The IR (KBr) shows a strong absorption at 2084 cm^{-1} due to the C≡C stretch motion, besides absorptions at 3384 (ν_{N-H}) and 1620 cm^{-1} (δ_{N-H}). The ^1H NMR shows a multiplet at 7.04–7.26 ppm due to the phenyl-protons and a singlet at 2.28 ppm, due to the NH_3 ligand. The signals due to the PMe_3 ligands appear at 1.65 (t, J = 2.9 Hz), 1.57 (d, J = 8.3 Hz) and 1.53 ppm (d, J = 6.8 Hz). These results as well as ^{31}P NMR spectrum, showing an A_2BC pattern, indicate the structure proposed in eq 3.



(3)

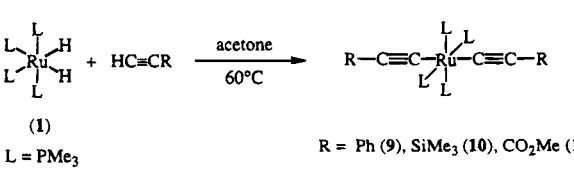
The exchange of NH_3 in **7** with CO leads to the formation of a moderately air- stable complex *cis*-[Ru(C≡CPh)(CO)(PMe_3)$_4$]PF_6 (**8**). The synthesis is best achieved by stirring an ether suspension of **7** for several hours at room temperature under a CO atmosphere. The yield is virtually quantitative. By treating *cis*-[RuH(NH_3)(PMe_3)$_4$]PF_6 (**2a**) with an excess of phenylacetylene, followed by stirring under a CO atmosphere for 4 h at room temperature, compound **8** was also obtained in good yield without isolation of **7**.

Formulation of **8** is supported by the IR spectrum in which, besides an absorption at 2104 cm^{-1} assigned to ν(C≡C), another very strong band at 1990 cm^{-1} (ν(CO)) is observed. The ^{13}C NMR shows the coordinated CO at 199.21 ppm (dtd, J = 74.8, 14.9 and 5.9 Hz).

No CO-insertion was observed, when a solution of **8** was stirred for 15 h at 60 °C. Even after reaction of **8** with pressurized CO (50 kg/cm^2, 60 °C, 15 h) the starting material was recovered almost quantitatively.

Reactions of the Neutral Dihydridoruthenium Complex 1 with Alkynes. In contrast to the ready reaction of the cationic hydridoruthenium complex **2a** with phenylacetylene heating was necessary to initiate the reactions of alkynes with the neutral complex **1**.

Reactions of **1** with HC≡CR (R = Ph, $SiMe_3$, CO_2Me) in acetone at 60 °C gives the bis(alkynyl)ruthenium complexes, *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$ (**9**), *trans*-Ru(C≡CSiMe_3)$_2$(PMe_3)$_4$ (**10**) and *trans*-Ru(C≡CCO_2Me)$_2$(PMe_3)$_4$ (**11**), respectively, in good yields.



(4)

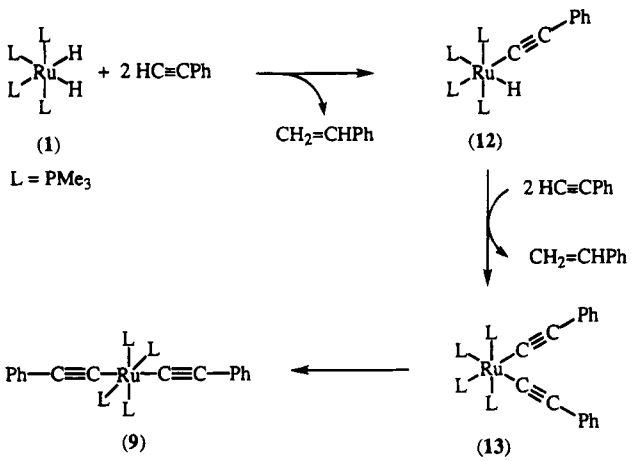
(1)

L = PMe_3

R = Ph (**9**), $SiMe_3$ (**10**), CO_2Me (**11**)

All the bis(alkynyl)ruthenium complexes were obtained as colorless solids that are insoluble in acetone

Scheme 1



and slightly soluble in dichloromethane. The complexes are moderately air-stable.

Since the IR spectra of **9**, **10** and **11** show only one C≡C stretching frequency at 2052 (**9**), 1988 (**10**), and 2005 cm^{-1} (**11**), respectively, we assume that the two alkynyl ligands are symmetrically coordinated. The NMR data (^1H, ^{13}C, ^{31}P NMR) are also consistent with the trans structure as shown in eq 4, in which the four phosphorus atoms are magnetically equivalent. The ^1H NMR show broad singlets at 1.55 (**9**), 1.55 (**10**) and 1.50 ppm (**11**), due to the PMe_3 ligands. In the ^{31}P NMR only one resonance at −4.53 (**9**), −7.78 (**10**) and −9.93 ppm (**11**), respectively, can be observed. The ^{13}C NMR spectra show broad singlets at 20.22 (**9**), 19.60 (**10**) and 19.56 ppm (**11**), due to the PMe_3 ligands. The C_α resonance in the Ru-C_α≡C_β-unit is observed at 132.45 (**9**), 157.45 (**10**) and 145.93 ppm (**11**), respectively, and C_β at 108.22 (**9**), 110.22 (**10**) and 101.98 ppm (**11**), which are split into quintets due to the P-C coupling.

In the reaction of the neutral complex **1** with phenylacetylene no apparent inhibition was observed by addition of extra PMe_3. Tolane did not react with **1** in acetone on heating at 60 °C for 15 h. These results suggest that the direct attack of the acidic phenylacetylene on the hydride complex **1** may be operative.[3h,4]

The ^1H and $^{31}P\{^1H\}$ NMR spectroscopic study of the reaction between **1** and phenylacetylene revealed involvement of intermediate species in the process converting **1** into **9**. When *cis*-$RuH_2(PMe_3)_4$ (**1**) was treated with phenylacetylene (ca. 2 equiv) at room temperature, the formation of the alkynyl(hydrido)ruthenium complex *cis*-RuH(C≡CPh)$(PMe_3)_4$ (**12**) and styrene can be observed after 10 min. Although **12** has not been isolated, the NMR spectra strongly support the structure suggested in Scheme 1. The presence of a hydride ligand is substantiated in the ^1H NMR spectra by a signal at −9.71 ppm (dq, J = 86.6 and 26.4 Hz). The triplet at 1.51 (J = 2.6 Hz) and the doublets at 1.36 (J = 5.9 Hz) and 1.31 ppm (J = 5.9 Hz) belong to the protons of the phosphine ligands. In the ^{31}P NMR spectrum an A_2BC spin system (δA = −3.56, δB = −14.61, δC = −6.08 ppm; J_{AB} = 24.9, J_{AC} = 31.5, J_{BC} = 23.5 Hz) can be observed. All these data are in agreement with the proposed structure *cis*-RuH(C≡CPh)$(PMe_3)_4$ (**12**).[15,17] Complex **12** further reacts slowly with the alkyne to give *cis*-Ru(C≡CPh)$_2(PMe_3)_4$ (**13**) and styrene. At room temperature the reaction is completed after 24 h. The ^1H NMR spectrum of **13** shows two triplets at 1.62 (t, J = 2.9 Hz, PMe_3) and 1.44 ppm (t, J = 3.7 Hz, PMe_3), respectively. The ^{31}P NMR shows an A_2B_2-spin system: δA = −5.90, δB = −9.56 ppm; J_{AB} = 30.0 Hz. The coupling pattern of the PMe_3 ligands is consistent with the cis-structure of the complex.[15,25] When a solution of **13** in acetone-d_6 was kept at 60 °C for 2 h, complex **13** was finally converted quantitatively into the trans-isomer *trans*-Ru(C≡CPh)$_2(PMe_3)_4$ (**9**). No further reaction of **9** with phenylacetylene (acetone-d_6, 60 °C, 2 d) could be observed.

In an exactly analogous sequence, *cis*-$RuH_2(PMe_3)_4$ (**1**) reacts with HC≡CSiMe$_3$ and HC≡CCO_2Me to give the corresponding bisalkynyl complexes **10** and **11** as confirmed by ^1H and ^{31}P NMR. In both cases the corresponding alkenes were detected (see also experimental part).

Acidolysis of *trans*-Ru(C≡CPh)$_2(PMe_3)_4$ (**9**) with an excess of trifluoro acetic acid in THF liberates (*Z*)-1,4-diphenylbuten-3-yne.

Catalytic Dimerization of Phenylacetylene to (*Z*)-1,4-Diphenylbuten-3-yne by 2a and 7. When *cis*-[RuH$(NH_3)(PMe_3)_4$]PF_6 (**2a**) was treated at room temperature with an excess of phenylacetylene we observed catalytic production of (*Z*)-1,4-diphenylbuten-3-yne [substrate to catalyst ratio 50; 0.5 mL of acetone, 5 h, 10% conversion]. At 60 °C the catalytic activity is significantly increased (90% conversion, *Z* isomer 90%, *E* isomer 10%; turnover number 40). Similar conversion (90%) and selectivity (82% in the *Z* isomer) are found for the catalytic dimerization of HC≡CPh to 1,4-diphenylbuten-3-yne by using **7** as catalyst.

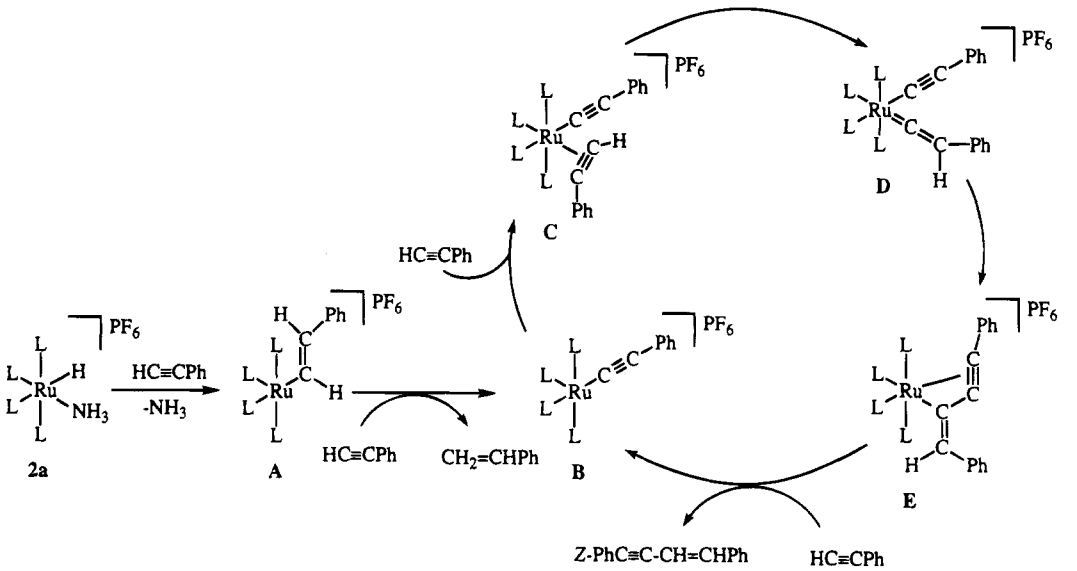
When complex **2a** was treated at 60 °C with an excess of HC≡CSiMe$_3$, the formation of $Me_3SiCH{=}CH_2$ and (*Z*)-$Me_3SiC{\equiv}C{-}CH{=}CHSiMe_3$ could be observed. A catalytic dimerization of HC≡CSiMe$_3$ was not possible under these conditions. The reaction of compound **2a** with HC≡CCO_2Me yields neither the alkene nor the enyne.

Discussion

In line with our previous observation that the reactivities of organopalladium complexes have been enhanced by creating cationic organopalladium complexes from neutral ones, conversion of the neutral hydrido ruthenium complex **1** into a cationic *cis*-monohydridoruthenium complex **2a** caused enhancement in the reactivity toward alkynes. While heating at 60 °C was required to have complex **1** react with alkynes to give stable and catalytically inactive bis(alkynyl) complexes **9**−**11**, the reaction of the cationic complex **2a** with phenylacetylene smoothly proceeds at room temperature to give *cis*-[Ru(C≡CPh)$(NH_3)(PMe_3)_4$]PF_6 (**7**). The both cationic complexes **2a** and **7** proved to be catalytically active to convert an excess alkyne into (*Z*)-1,4-diphenylbuten-3-yne at 60 °C.

Monitoring the reaction of the hydrido complex **2a** with phenylacetylene by ^1H NMR showed the presence of two organometallic species in the course of the catalysis, suggesting involvement of such complexes in the catalytic process. The spectroscopic data of one of the two intermediates (**B**) (see Scheme 2) are in accordance with the σ-alkynyl complex **7**. The other complex, which may correspond to complex **E** in Scheme 2, has a ligand with a strong π-acceptor ability as far as one can judge from the chemical shift of the equato-

Scheme 2



[a] L = PMe_3.

rial PMe_3 ligands at 1.82 (d, J = 8.6 Hz) and 1.78 ppm (d, J = 6.9 Hz), respectively. A similar chemical shift was observed for *cis*-[Os(η^3-PhC_3=CHPh)(PMe_3)$_4$]PF_6.[18]

A possible reaction pathway of the catalytic dimerization is outlined in Scheme 2. Starting from the hydrido complex **2a**, the σ-alkenyl complex **A** may be formed. The reaction of **A** with phenylacetylene to give the alkynyl species **B** is probably very fast, because the σ-alkenyl complex could not be observed by ^{1}H NMR, even when 1 equiv of phenylacetylene was used. Complex **B** may then react with further alkyne to form the alkynyl(alkyne) complex **C**. Once the alkynyl complex coordinated with alkyne **C** has rearranged into an alkynyl(vinylidene) complex **D**, the PhC_3CHPh ligand may be formed via C-C bond formation between the α-carbon of vinylidene and the alkynyl ligand. The PhC_3CHPh ligand in **E** will then accept hydrogen from a newly coordinating alkyne to be freed as (*Z*)-1,4-diphenylbuten-3-yne, with regeneration of the original alkynyl intermediate **B**. The mechanism suggested in Scheme 2 is in accordance with the observations of other groups.[4d,e]

In accord with the proposed mechanism, when the coordination site in the σ- alkynyl complex **B** is saturated with CO, the six-coordinated complex *cis*-[Ru(C≡CPh)(CO)(PMe_3)$_4$]PF_6 **8** is formed and no further reaction with 1-alkynes occurs. Similarly, when the reaction of phenylacetylene with complex **2a** and **7**, respectively, was carried out under an NH_3-atmosphere no catalytic dimerization could be observed.

The catalytic activity decreases with time and the dimerization process finally stops. When the reaction mixture was worked up, the only isolated organometallic species was *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$ (**9**). The yield was almost quantitative. The results suggest that *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$ (**2**) is not catalytically active and its formation leads to a halt of the catalytic cycle. This may happen from the supposed alkynyl(vinylidene) species **D** (see Scheme 3). After isomerization from the cis- into the trans-configuration, the deprotonation of **F** would lead to *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$ (**9**). The reverse reaction is possible as shown in Scheme 3. If **9** is treated with an acid, such as CF_3COOH, (*Z*)-1,4-diphenylbuten-3-yne is liberated, possibly through a route **9** → **F** → **D** → **E** to the enyne.

We have examined also the reactivity of the PPh_3-coordinated complexes *cis*- $RuH_2(PPh_3)_4$ (**14**)[11] and [RuH(PPh_3)$_4$]PF_6[19] toward phenylacetylene. In various catalytic reactions PPh_3-coordinated complexes are known to serve as more efficient catalyst than PMe_3-coordinated complexes, because the PPh_3 ligand is only weakly coordinated and is easily exchanged with other substrates. The neutral complex **14** reacts in acetone at room temperature with phenylacetylene to give a complex product mixture. No identifiable organometallic species was produced in the reaction system and enyne was not detected. The cationic species [RuH(PPh_3)$_4$]PF_6 does not react with phenylacetylene at room temperature in acetone-d_6, but rearranges via [RuH(PPh_3)$_3$]PF_6 (RuH: −7.77 td, J = 103.5 and 25.9 Hz), into the previously described 18-electron complex [RuH(η^6-C_6H_5-PPh_2)(PPh_3)$_2$]PF_6 (RuH: −8.61, td, J = 38.8 and 8.5 Hz),[19] as confirmed by ^{1}H NMR. In a polar solvent such as acetonitrile [RuH(PPh_3)$_4$]PF_6 reacts at room temperature within a few minutes to give [RuH($NCCH_3$)$_2$-(PPh_3)$_3$]PF_6 (RuH: −13.68, q, J = 22.0 Hz, acetone-d_6). No dimerization of phenylacetylene was initiated by [RuH($NCCH_3$)$_2$(PPh_3)$_3$]PF_6 (acetone-d_6, 4h, 50 °C).

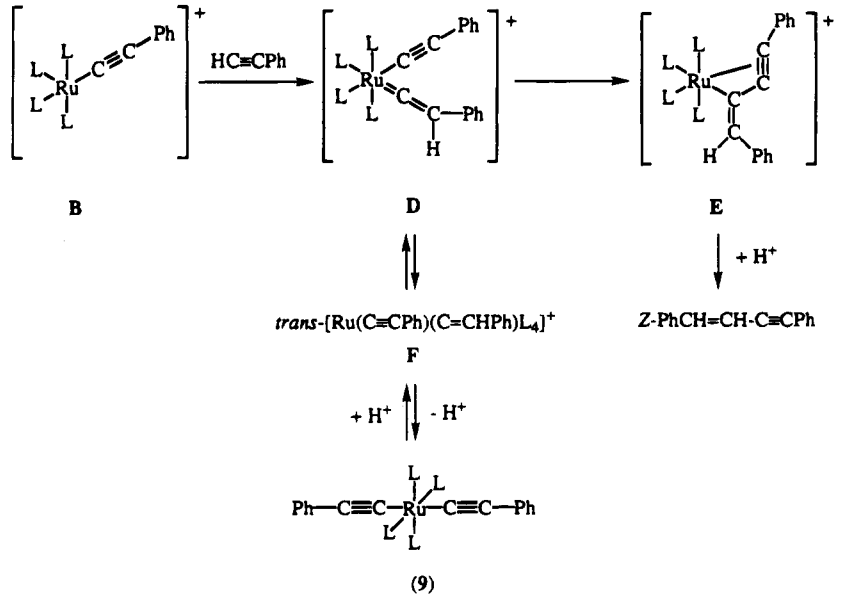
We have also included olefins in our comparative study. Hydrido- and olefin-coordinated complexes of transition metals are generally regarded as active intermediates in catalytic transformations of olefins.[20] For instance, complex **14** is used as a catalyst in a wide range of reactions, such as hydrogenation,[21] hydro-

(18) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247.

(19) Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **1973**, 743.

(20) See for example: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (c) Quirk, R. P. *Transition Metal Catalyzed Polymerization: Ziegler-Natta and Metathesis Polymerization*; Cambridge Press: Cambridge, 1988. (d) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986.

Scheme 3



[a] L = PMe_3.

formylation,[22] and C-C-coupling.[23] The complex **14** also initiates the vinyl polymerization[24] or forms π-complexes with a wide range of vinyl compounds.[25]

The PMe_3-coordinated complex **1** initiated the polymerization of acrylonitrile, methacrylonitrile and methylvinylketone, whereas with methyl acrylate, methyl methacrylate and styrene no reaction could be observed. In an independent experiment, however, it could be shown, that free PMe_3 itself initiates a quite rapid polymerization of acrylonitrile, methacrylonitrile and methylvinylketone. Because of the inherent possibility that the polymerization of the monomers was caused by the free PMe_3 released from **1**, further study of the reactions of **1** with the olefins was abandoned.

The cationic complexes *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ (**2a**) and *cis*-$[RuH(NCCH_3)(PMe_3)_4]PF_6$ (**3a**) do not initiate the polymerization of acrylonitrile.

Experimental Section

General Considerations. All reactions were carried out under argon atmosphere using standard Schlenk techniques. *cis*-$RuH_2(PPh_3)_4$,[11] *cis*-$[RuH(PPh_3)_4]PF_6$,[19] *cis*-$RuH_2(PMe_3)_4$,[9] and PMe_3[26] were prepared according to the literature.

Elemental analysis was carried out by using Yanako MT-3 (combustion-gas chromatograph system). NMR spectra were recorded at room temperature on a HITACHI R-90H (^1H, 90 MHz) or a JEOL EX-270 spectrometer (^1H, 270 MHz; ^{13}C, 100.5 MHz; ^{31}P, 109.4 MHz). ^1H and ^{13}C signals are referred to $SiMe_4$ as an internal standard and ^{31}P NMR signals to 85% H_3PO_4 as an external reference. IR spectra were recorded on a HITACHI I-3000 spectrophotometer.

Preparation of *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ (2a). To a solution of *cis*-$RuH_2(PMe_3)_4$ (**1**) (114 mg, 0.28 mmol) in 2 mL of Et_2O under a stream of NH_3 was added NH_4PF_6 (46 mg, 0.28 mmol). The solution was stirred for 90 min at room temperature. During this period a colorless solid precipitated, which was filtered, washed several times with Et_2O and dried in vacuo. Yield: 148 mg (93%). Anal. Calcd for $C_{12}H_{40}F_6NP_5Ru$ (568.30): C, 25.36; H, 7.04; N, 2.46. Found: C, 24.98; H, 7.27; N, 2.41. IR (KBr): ν(NH) 3408, ν(RuH) 1848, δ(NH) 1628 cm^{-1}.

In an analogous way *cis*-$[RuH(NH_3)(PMe_3)_4]BPh_4$ (**2b**) could be synthesized, starting from **1** (175 mg, 0.43 mmol) and NH_4BPh_4 (145 mg, 0.43 mmol). Yield 241 mg (75%). IR (KBr): ν(NH) 3388, ν(RuH) 1810, δ(NH) 1616 cm^{-1}.

Reaction of *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ (2a) with NaH and $NaBH_4$, Respectively. (a) To a solution of **2a** (325 mg, 0.60 mmol) in 20 mL of THF was added NaH (200 mg, 8.32 mmol). Spontaneously gas was evolved. The solution was stirred for 30 min at room temperature. Volatile materials were removed under vacuum and the residue was dissolved in 20 mL of a benzene/hexane(1:1)-mixture. Evaporation of the filtered solution yielded crude *cis*-$RuH_2(PMe_3)_4$,[9] which was purified by sublimation (90 °C, 10^{-2} torr). Yield: 143 g (58%).

(b) To a solution of **2a** (160 mg, 0.29 mmol) in 10 mL of acetone was added $NaBH_4$ (100 mg, 2.63 mmol). Spontaneously gas was evolved. The residue was extracted with benzene (10 mL) and the solution was filtered. Evaporation of the solution to ca. 2 mL, addition of 10 mL of Et_2O and cooling (−70 °C) yielded pale yellow crystals. These were collected, dried and characterized as $RuH(\eta^2\text{-}BH_4)(PMe_3)_3$.[9] On treatment with 1 equiv of PMe_3 in benzene at room temperature complex $RuH(\eta^2\text{-}BH_4)(PMe_3)_3$ can be converted into *cis*-$RuH_2(PMe_3)_4$.

Preparation of *cis*-$[RuH(NCCH_3)(PMe_3)_4]PF_6$ (3a). (a) *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ (**2a**) (82 mg, 0.15 mmol) was dissolved in 1 mL of CH_3CN and stirred for 30 min. Addition of 10 mL of Et_2O led to the precipitation of a colorless solid, which was filtered, washed several times with Et_2O and dried in vacuo. Yield: 79 mg (92%).

(b) To a solution of *cis*-$RuH_2(PMe_3)_4$ (**1**) (481 mg, 1.18 mmol) in 2 mL of CH_3CN was added NH_4PF_6 (182 mg, 1.12 mmol). Spontaneous gas evolution occurred. The solution was stirred for 30 min at room temperature, then concentrated to ca. 1 mL in vacuo and treated with 10 mL of Et_2O. A colorless solid

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precipitated, which was filtered, washed several times with Et_2O and dried in vacuo. Yield 610 mg (92%). Anal. Calcd for $C_{14}H_{40}F_6NP_5Ru$ (592.30): C, 28.39; H, 6.81; N, 2.36. Found: C, 28.01, 6.99, N, 2.33. IR (KBr): ν(CN) 2284, ν(RuH) 1838 cm^{-1}.

In an analogous way *cis*-[RuH($NCCH_3$)(PMe_3)$_4$]BPh_4 (**3b**) could be synthesized, starting from **1** (96 mg, 0.24 mmol) and NH_4BPh_4 (79 mg, 0.24 mmol). Yield 123 mg (67%). IR (KBr): ν(CN) 2284, ν(RuH) 1814 cm^{-1}.

Preparation of *cis*-[Ru(NH_3)$_2$(PMe_3)$_4$][PF_6]$_2$ (4). To a solution of *cis*-$RuH_2(PMe_3)_4$ (**1**) (120 mg, 0.29 mmol) in 3 mL of acetone was added NH_4PF_6 (96 mg, 0.60 mmol). Gas was evolved spontaneously. The solution was stirred for 15 min at room temperature, then concentrated to ca. 1 mL in vacuo and treated with 10 mL of Et_2O. A colorless solid precipitated, which was filtered, washed several times with Et_2O and dried in vacuo. Yield 142 mg (67%). Anal. Calcd for $C_{12}H_{42}F_{12}N_2P_6Ru$ (729.53): C, 19.76; H, 5.80; N, 3.84. Found: C, 20.16, H, 6.19, N, 3.35. IR (KBr): ν(NH) 3372, δ(NH) 1624 cm^{-1}.

Preparation of *cis*-[Ru($NCCH_3$)$_2$(PMe_3)$_4$][PF_6]$_2$ (5a). (a) *cis*-[Ru(NH_3)$_2$(PMe_3)$_4$][PF_6]$_2$ (**4**) (95 mg, 0.13 mmol) was dissolved in 1 mL of CH_3CN and stirred for 30 min. Addition of 10 mL of Et_2O led to the precipitation of a colorless solid, which was filtered, washed several times with Et_2O and dried in vacuo. Yield: 81 mg (94%).

(b) To a solution of *cis*-$RuH_2(PMe_3)_4$ (**1**) (117 mg, 0.298 mmol) in 3 mL of CH_3CN was added NH_4PF_6 (94 mg, 0.58 mmol) to cause spontaneous release of a gas. The solution was stirred for 15 min at room temperature, then concentrated to ca. 1 mL in vacuo and treated with 10 mL of Et_2O. A colorless solid precipitated, which was filtered, washed several times with Et_2O and dried in vacuo. Yield 140 mg (62%). Anal. Calcd for $C_{16}H_{42}F_{12}N_2P_6Ru$ (777.40): C, 24.72; H, 5.44; N, 3.60. Found: C, 25.07, 5.41, N, 4.09. IR (KBr): ν(CN) 2288 cm^{-1}.

In an analogous way *cis*-[Ru($NCCH_3$)$_2$(PMe_3)$_4$][BF_4]$_2$ (**5b**) could be synthesized, starting from **1** (230 mg, 0.56 mmol) and HBF_4·OEt_2 (150 μL, 1.20 mmol). Yield 211 mg (57%). Anal. Calcd for $C_{16}H_{42}B_2F_8N_2P_4Ru$ (661.20): C, 29.06; H, 6.40; N, 4.23. Found: C, 29.04, 6.31, N, 4.53. IR (KBr): ν(CN) 2288 cm^{-1}.

Preparation of *cis*-[RuH(CO)(PMe_3)$_4$]PF_6 (6). *cis*-[RuH(NH_3)(PMe_3)$_4$]PF_6 (**2a**) (164 mg, 0.29 mmol) was dissolved in 2 mL of acetone and the solution was stirred under a CO atmosphere for 3 h at room temperature. Addition of 10 mL of Et_2O led to the precipitation of a colorless solid, which was filtered, washed several times with Et_2O and dried in vacuo. Yield: 158 mg (94%). cis-[RuH(CO)(PMe_3)$_4$]PF_6 (**6**) is also formed, if a solution of **3a** (70 mg, 0.12 mmol) in 2 mL of acetone is stirred under a CO atmosphere for 24 h at room temperature. Yield: 63 mg (91%). Anal. Calcd for $C_{13}H_{37}F_6OP_5Ru$ (579.36): C, 26.95; H, 6.43. Found: C, 26.78; H, 6.67. IR (KBr) ν(CO) 1950, ν(RuH) 1880 cm^{-1}.

Preparation of *cis*-[Ru(C≡CPh)(NH_3)(PMe_3)$_4$]PF_6 (7). To a solution of *cis*-[RuH(NH_3)(PMe_3)$_4$]PF_6 (**2a**) (235 mg, 0.41 mmol) in 3 mL of acetone was added HC≡CPh (91 μL, 0.82 mmol). The solution was stirred for 3 h at room temperature. During this period the solution changed from colorless to pale yellow. The solution was concentrated in vacuo, 10 mL of Et_2O was added and then stored overnight at −78 °C. Colorless crystals precipitated, which were filtered, washed several times with Et_2O and dried in vacuo. Yield: 101 mg (37%). Anal. Calcd for $C_{20}H_{44}F_6NP_5Ru$ (668.43): C, 35.93; H, 6.63; N, 2.09. Found: C, 35.91; H, 6.90; N, 2.02. IR (KBr): ν(NH) 3384, ν(C≡C) 2084, δ(NH) 1620 cm^{-1}.

Preparation of *cis*-[Ru(C≡CPh)(CO)(PMe_3)$_4$]PF_6 (8). (a) A solution of *cis*-[RuH(NH_3)(PMe_3)$_4$]PF_6 (**2a**) (46 mg, 0.08 mmol) in 2 mL of acetone was treated with PhC≡CH (100 μL, 0.91 mmol) and stirred for 15 min at room temperature. Then 10 mL of Et_2O was added and the mixture was stirred under a CO atmosphere for 4 h. During this time a colorless solid precipitated, which was filtered, washed several times with Et_2O and dried in vacuo. Yield: 37 mg (68%).

(b) A suspension of *cis*-[Ru(C≡CPh)(NH_3)(PMe_3)$_4$]PF_6 (**7**) (56 mg, 0.08 mmol) in 10 mL of Et_2O was stirred under a CO atmosphere for 13 h at room temperature. The colorless solid was then filtered, washed several times with Et_2O and dried in vacuo. Yield: 52 mg (96%). Anal. Calcd for $C_{21}H_{41}F_6OP_5Ru$ (679.50): C, 37.11; H, 6.08. Found: C, 37.38; H, 6.43. IR (KBr): ν(C≡C) 2104, ν(CO) 1990 cm^{-1}.

Preparation of *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$ (9). PhC≡CH (141 μL, 1.28 mmol) was added to a solution of *cis*-$RuH_2(PMe_3)_4$ (**1**) (130 mg, 0.32 mmol) in 3 mL of acetone. After 2 h of stirring at 60 °C, white crystals precipitated from the solution, which were filtered off, washed with cold acetone and Et_2O and dried in vacuo. This yielded *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$ (**9**) (85 mg, 44%) in colorless, air-stable crystals. Anal. Calcd for $C_{28}H_{46}P_4Ru$ (606.7): C, 55.34; H, 7.63. Found: C, 54.92; H, 7.68. IR (KBr): ν(C≡C) 2052 cm^{-1}.

Preparation of *trans*-Ru(C≡CSiMe_3)$_2$(PMe_3)$_4$ (10). To an acetone (3 mL) solution of *cis*-$RuH_2(PMe_3)_4$ (**1**) (125 mg, 0.31 mmol) was added HC≡CSiMe_3 (200 μL, 1.43 mmol). After reaction for 30 min at 60 °C colorless, moderately air-stable crystals precipitated, which were filtered off, washed with Et_2O and dried in vacuo. Yield: 115 mg (65%). Anal. Calcd for $C_{22}H_{54}Si_2P_4Ru$ (599.80): C, 44.05; H, 9.07. Found: C, 44.61; H, 9.07. IR (KBr): ν(C≡C) 1988 cm^{-1}.

Preparation of *trans*-Ru(C≡CCO_2Me)$_2$(PMe_3)$_4$ (11). To an acetone (2 mL) solution of *cis*-$RuH_2(PMe_3)_4$ (**1**) (63 mg, 0.15 mmol) was added HC≡CCO_2Me (100 μL, 1.19 mmol). After stirring for 15 h at 60 °C the reaction mixture was cooled to room temperature to give colorless crystals, which were filtered off, washed with Et_2O and dried in vacuo. Yield: 19 mg (21%). Anal. Calcd for $C_{20}H_{40}O_4P_4Ru$ (571.51): C, 42.03; H, 7.05. Found: C, 41.85; H, 7.22. IR (KBr): ν(C≡C) 2005, ν(C=O) 1723, ν(C−O−C) 1210 cm^{-1}.

NMR Study of the Reaction of *cis*-$RuH_2(PMe_3)_4$ (1) with Phenylacetylene. (a) An NMR tube containing *cis*-$RuH_2(PMe_3)_4$ (**1**) (20 mg, 0.05 mmol) and acetone-d_6 (0.5 mL) was capped with a rubber septum under argon. Phenylacetylene (10 μL, 0.09 mmol) was introduced with a syringe. The ^{1}H NMR spectrum after the reaction at room temperature for 10 min shows styrene and a new hydridoruthenium complex *cis*-RuH(C≡CPh)(PMe_3)$_4$ (**12**) besides the signals for the starting material. The same result was obtained at −60 °C, whereas the formation of an alkenyl species was not observed. After the NMR measurement additional phenylacetylene (20 μL, 0.18 mmol) was introduced with a syringe. The ^{1}H NMR spectrum observed after 1 and 3 h, respectively, showed the decrease in the peak area of **12** and an increase of styrene. The signals of **12** disappeared completely after reaction at room temperature for 24 h to give a new set of signals [*cis*-Ru(C≡CPh)$_2$(PMe_3)$_4$ (**13**)]. When the NMR tube was heated at 60 °C for 2 h, complex **13** was transformed quantitatively into *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$ (**9**). No further reaction of **9** with phenylacetylene was observed over a period of 2 d at 60 °C.

(b) The reaction of *cis*-$RuH_2(PMe_3)_4$ (**1**) with phenylacetylene was also examined in the presence of PMe_3. A mixture of **1** (20 mg, 0.05 mmol), phenylacetylene (30 μL, 0.27 mmol) and PMe_3 (100 μL, 0.97 mmol) in acetone-d_6 (0.5 mL) was sealed in an NMR-tube. After 2 h at 60 °C, complex **1** was transformed quantitatively into *trans*-Ru(C≡CPh)$_2$(PMe_3)$_4$ (**9**).

NMR Study of the Reaction of *cis*-$RuH_2(PMe_3)_4$ (1) with HC≡CSiMe_3 and HC≡CCO_2Me, Respectively. (a) An NMR tube containing *cis*-$RuH_2(PMe_3)_4$ (**1**) (20 mg, 0.05 mmol) and acetone-d_6 (0.5 mL) was capped with a rubber septum under argon. Trimethylsilylacetylene (7 μL, 0.10 mmol) was introduced with a syringe. The ^{1}H NMR spectra observed after reaction at room temperature for 10 min and 40 min, respectively, show only the signals for the starting material. The mixture was then heated for 30 min at 60 °C. Besides the signals arising from the starting material and $Me_3SiCH{=}CH_2$, a new hydride species (Ru−H: −9.63 dq, J = 84.7 and 26.0 Hz) could be observed. In the ^{31}P NMR spectra we observed four organometallic species: the starting complex **1**, a L_4RuXY-

species, which may correspond to *cis*-$RuH(C{\equiv}CSiMe_3)(PMe_3)_4$ (A_2BC-spin-system: $\delta A = -3.72$, $\delta B = -15.35$, $\delta C = -5.62$ ppm; $J_{AB} = 24.2$, $J_{AC} = 31.0$, $J_{BC} = 25.6$ Hz), a L_4RuX_2-species, which may correspond to *cis*-$Ru(C{\equiv}CSiMe_3)_2(PMe_3)_4$ (A_2B_2-spin-system: $\delta A = -10.44$, $\delta B = -14.15$ ppm; $J_{AB} = 30.0$ Hz) and a singlet at -7.76 ppm for complex **10**. After the NMR measurement additional trimethylsilylacetylene (15 μL, 0.20 mmol) was introduced via syringe. The ^{31}P NMR spectrum after reaction at 60 °C for 2 h shows only the A_2B_2-spin-system and the signal arising from compound **10**. After 24 h at 60 °C the mixture was transformed quantitatively into *trans*-$Ru(C{\equiv}CSiMe_3)_2(PMe_3)_4$ (**10**).

(b) The reaction of *cis*-$RuH_2(PMe_3)_4$ (**1**) with 5 equiv of $HC{\equiv}CCO_2Me$ at room temperature after 10 min leads to a complex mixture. In the ^{31}P NMR spectra we observe four organometallic species: the starting complex **1**, a L_4RuXY-species, which may correspond to *cis*- $RuH(C{\equiv}CCO_2Me)(PMe_3)_4$ (A_2BC-spin-system: $\delta A = -5.95$, $\delta B = -16.87$, $\delta C = -10.32$ ppm; $J_{AB} = 24.1$, $J_{AC} = 32.1$, $J_{BC} = 26.1$ Hz), a L_4RuX_2-species, which may correspond to *cis*-$Ru(C{\equiv}CCO_2Me)_2(PMe_3)_4$ (A_2B_2-spin-system: $\delta A = -10.85$, $\delta B = -14.31$ ppm; $J_{AB} = 30.3$ Hz) and a singlet at -9.87 ppm for complex **11**. After 15 h at 60 °C the mixture was transformed quantitatively into *trans*-$Ru(C{\equiv}CCO_2Me)_2(PMe_3)_4$ (**11**).

Acidolysis of *trans*-$Ru(C{\equiv}CPh)_2(PMe_3)_4$ (9). A solution of *trans*- $Ru(C{\equiv}CPh)_2(PMe_3)_4$ (**9**) (40 mg, 0.07 mmol) in 0.5 mL of acetone was treated with CF_3COOH (12 μL, 0.16 mmol) and the solution was heated for 3 h at 60 °C. During this time a color change from colorless via pink to orange/yellow occurred and *Z*–PhCH=CHC≡CPh [2b,c] was detected by ^1H NMR spectroscopy.

Catalytic Dimerization of Phenylacetylene by *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ (2a) and *cis*-$[Ru(C{\equiv}CPh)(NH_3)(PMe_3)_4]PF_6$ (7), Respectively. (a) A mixture of **2a** (60 mg, 0.09 mmol) and phenylacetylene (1 mL, 9.11 mmol) in 2 mL of acetone was heated for 3 h at 60 °C. The mixture was then cooled to room temperature and concentrated by evaporation, and the residue was chromatographed over silica gel (Et_2O) to give (*Z*)-1,4- diphenylbuten-3-yne (85%) and (*E*)-1,4-diphenylbuten-3-yne (15%) as an oil (yield: 385 mg, 38%) [2b,c].

(b) A mixture of **2a** (19 mg, 0.03 mmol) and phenylacetylene (150 μL, 1.37 mmol) in 0.5 mL of acetone-d_6 was sealed in an NMR-tube. Every hour the mixture was checked with ^1H NMR. After 5 h ca. 10% of the alkyne was converted into (*Z*)-1,4-diphenylbuten-3-yne. The mixture was then heated at 60 °C for 3 h. After this period a conversion of 90% was reached. The product ratio of the *Z* isomer to *E* isomer was 9:1. The mixture was then no longer catalytically active.

(c) A mixture of **7** (20 mg, 0.03 mmol) and phenylacetylene (150 μL, 1.37 mmol) in 0.5 mL of acetone-d_6 was sealed in an NMR-tube. Every hour the mixture was checked with ^1H NMR. After 5 h ca. 10% of the alkyne was converted into *Z*-1,4-diphenylbuten-3-yne. The mixture was then heated at 60 °C for 3 h. After the period a conversion of 90% was reached to give 1,4-diphenylbuten-3–yne in an E/Z ratio of 82:18.

(d) A mixture of **2a** (20 mg, 0.03 mmol) and phenylacetylene (150 μL, 1.37 mmol) in 0.5 mL of acetone-d_6 was saturated with NH_3 and sealed in an NMR tube. Every hour the mixture was checked with ^1H NMR. After 5 h at room temperature and also after the mixture was heated at 60 °C for 3 h no enyne could be detected.

Reaction of *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ (2a) with $HC{\equiv}CSiMe_3$ and $HC{\equiv}CCO_2Me$, Respectively. (a) A mixture of **2a** (20 mg, 0.03 mmol) and trimethysilylacetylene (140 μL, 2.00 mmol) in 0.5 mL of acetone-d_6 was sealed in an NMR-tube. After 10 min at room temperature $Me_3SiCH{=}CH_2$ was detected. The formation of the enyne could not be observed at room temperature within 3 h, whereas heating at 60 °C for 1 h gave $Me_3SiC{\equiv}C{-}CH{=}CHSiMe_3$. A catalytic dimerization of $HC{\equiv}CSiMe_3$ was not observed after 12 h at 60 °C.

(b) When **2a** was treated with an excess of $HC{\equiv}CCO_2Me$ and heated at 60 °C for 3 h neither $H_2C{=}CHCO_2Me$ nor $MeO_2CC{\equiv}C{-}CH{=}CHCO_2Me$ could be detected.

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