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A novel bifunctional bridging phosphinomethyl-alkoxycarbene ligand from (diphenylphosphinoacetylene)-ruthenium complexes

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Abstract

Some new neutral and cationic [HC≡C(Ph$_2$)P](η^6-arene)ruthenium(II) complexes have been prepared, namely (η^6-arene)Cl$_2$RuP(Ph$_2$)C≡CH and [(η^6-arene)(L)ClRuP(Ph$_2$)C≡CH]$^+$ (L = PMe$_3$, SMe$_2$). Activation of the terminal alkyne function allowed formation of unsymmetrical dinuclear derivatives in a process involving formation of a bridging phosphino-methoxycarbene ligand.

Introduction

Metal coordination compounds of phosphinoalkynes have been shown to be precursors of η^2-phosphinoenolato complexes by addition of water to the C≡C triple bond [1] and of (η^2-phosphinothioenolato)complexes by coupling with CS$_2$ [2]. In the course of our studies of (η^2-phosphinoenolato)(η^6-arene)ruthenium(II) derivatives containing functional phosphine ligands [3], we decided to study the activation of diphenylphosphinoacetylene, Ph$_2$PC≡CH, (dpa) linked to an (arene)Ru^{II} moiety. We show below that transformation of the C≡CH function to a methoxycarbene ligand provides a route to dinuclear ruthenium complexes.

Results and discussion

The reaction of dpa with dinuclear ruthenium complexes [(η^6-arene)RuCl$_2$]$_2$ in dichloromethane leads to derivatives of type **1**, containing the free C≡CH group, by the reaction shown in eq. 1.

$$[(\eta^6\text{-arene})RuCl_2]_2 + 2Ph_2PC{\equiv}CH \longrightarrow 2(\eta^6\text{-arene})Ru(Cl)_2P(Ph_2)C{\equiv}CH \quad (1)$$

(1)

(**1a** arene = 1,3,5-Me$_3$C$_6$H$_3$;
1b arene = *p*-MeC$_6$H$_4$CHMe$_2$)

Table 1

Analytical data for the arene–ruthenium complexes

Complex	Analyses (Found (Calc.)) (%)				
	C	H	Cl	S	P
(1,3,5-$Me_3C_6H_3$)Cl_2RuP(Ph_2)C≡CH (**1a**)	54.70	4.67	14.61		6.03
	(54.99)	(4.61)	(14.11)		(6.17)
(*p*-$MeC_6H_4CHMe_2$)Cl_2RuP(Ph_2)C≡CH (**1b**)	55.84	4.91	13.89		5.89
	(55.82)	(4.88)	(13.73)		(6.00)
[(C_6Me_6)(PMe_3)ClRuP(Ph_2)C≡CH](PF_6) (**2**)	47.45	5.17	5.84		12.90
	(47.71)	(5.25)	(4.86)		(12.73)
[(1,3,5-$Me_3C_6H_3$)(SMe_2)ClRuP(Ph_2)C≡CH](PF_6) (**3**)	44.76	4.11	6.09	5.90	9.06
	(44.55)	(4.34)	(5.26)	(4.76)	(9.19)
{(*p*-$MeC_6H_4CHMe_2$)Cl_2Ru[μ-P(Ph_2)CH_2C(OMe)]-Ru(Cl)(PMe_3)(C_6Me_6)}(PF_6) (**4**)					
	44.82	5.29	10.14		8.58
	(44.97)	(5.28)	(9.96)		(8.70)

Addition of diethyl ether to the resulting red solution induces crystallization of the red compounds **1a** and **1b** (86%). However, **1a** is better prepared by mixing dichloromethane solutions of dpa and of the soluble complex (η^6-1,3,5-$Me_3C_6H_3$)(SMe_2)Cl_2Ru [4] containing the labile SMe_2 ligand. In this case, the red precipitate of pure **1a** (75%) arises from the ligand exchange reaction shown in eq. 2:

$$(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)\text{Cl}_2\text{Ru(SMe}_2) + \text{Ph}_2\text{PC}{\equiv}\text{CH} \longrightarrow (\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)\text{Cl}_2\text{RuP(Ph}_2)\text{C}{\equiv}\text{CH} + \text{SMe}_2 \quad (2)$$

(1a)

Complexes **1a** and **1b** were fully characterized by elemental analysis (Table 1), IR and NMR (Table 2) spectroscopy. The IR spectra of **1a** and **1b** show a characteristic C≡C absorption at 2044 cm^{-1}. The ^{31}P NMR spectra show a single resonance at $\delta = 6.2$ ppm (**1a**) and $\delta = -0.2$ ppm (**1b**). The ^1H NMR spectra show the resonance of the acetylenic proton as a doublet at $\delta = 3.65$ ppm (**1a**) and $\delta = 3.72$ ppm (**1b**), with coupling constants ^3J(PH) of 7.3 Hz and 7.6 Hz respectively.

In order to evaluate the ability of dpa to serve as a functional terminal alkyne capable of being activated by ruthenium(II) moieties, the reactivity of dpa towards (η^6-C_6Me_6)(PMe_3)$RuCl_2$ has been investigated. With $NaPF_6$ (or NH_4PF_6) in methanol, under the conditions used for the formation of methoxycarbene-ruthenium derivatives [5], the reaction leads selectively to a cationic derivative **2** by displacement of the chloride ligand (eq. 3):

$$(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{Cl})_2(\text{PMe}_3) + \text{Ph}_2\text{PC}{\equiv}\text{CH} + \text{MPF}_6\ (\text{M} = \text{Na, NH}_4) \longrightarrow \left[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{Cl})(\text{PMe}_3)(\text{P(Ph}_2)\text{C}{\equiv}\text{CH})\right]^+ (\text{PF}_6)^- \quad (3)$$

(2)

Table 2

^1H and ^{31}P NMR [a] data for the arene–ruthenium complexes

Complex (yield, %)	^1H NMR, δ (ppm)		^{31}P NMR, δ (ppm)
	Arene ligand	Other ligands	
1a	4.80 s, 3H, C_6H_3	7.93–7.34 m, 10H, Ph	6.8
(75)	2.01 s, 9H, C_6Me_3	3.63 d, 1H, HC≡	
		^3J(PH) = 7.4 Hz	
1b	5.30 dd, 4H, C_6H_4	7.99–7.42 m, 10H, Ph	−0.2
(86)	2.81 m, 1H, $CH(Me_2)$	3.72 d, 1H, HC≡	
	1.96 s, 3H, Me(Ar)	^3J(PH) = 7.6 Hz	
	1.18 d, 6H, Me_2C		
	^3J(HH) = 7.1 Hz		
2	1.88 s, 18H, C_6Me_6	8.03–7.32 m, 10H, Ph	15.9 d PPh_2
(69)		4.13 d, 1H, HC≡	6.5 d PMe_3
		^3J(PH) = 7.7 Hz	^2J(PP) = 64 Hz
		1.16 d, 9H, PMe_3	
		^2J(PH) = 10.5 Hz	
3	5.22 s, 3H, C_6H_3	8.18–7.35 m, 10H, Ph	12.1
(75)	2.10 s, 9H, C_6Me_3	4.15 d, 1H, HC≡	
		^3J(PH) = 7.9 Hz	
		2.12 s, 3H, SMe	
		2.09 s, 3H, SMe	
4 [b]	5.47 dd, 2H, C_6H_4	8.04–7.50 m, 10H, Ph	23.3 d PPh_2
(37)	^3J(HH) = 6.2 Hz	4.70 d, 1H, CH_2	6.0 d PMe_3
	4.98 dd, 2H, C_6H_4	^2J(HH) = 19.8 Hz	^4J(PP) = 10 Hz
	^3J(HH) = 5.6 Hz	4.53 d(dd), 1H, CH_2	
	2.28 m, 1H, $CH(Me_2)$	J(PH) = 8.7 Hz, 2.1 Hz	
	1.89 s, 3H, Me(Ar)	4.48 s, 3H, OMe	
	1.77 s, 18H, C_6Me_6	1.58 d, 9H, PMe_3	
	1.01 d, 3H, $CMe_{(2)}$	^2J(PH) = 9.0 Hz	
	^3J(HH) = 7.0 Hz		
	0.49 d, 3H, $CMe_{(2)}$		
	^3J(HH) = 6.9 Hz		

[a] In CD_2Cl_2, 300.134 MHz (^1H) and 121.496 MHz (^{31}P), 297 K. [b] Major isomer.

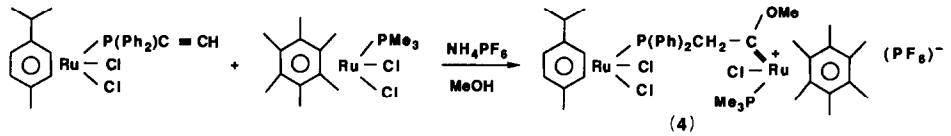
The structure of **2** was established from its NMR data (Table 2) in particular the observation of ^2J(PP) coupling (64 Hz) in the ^{31}P NMR spectrum. The retention of the free acetylenic function was also shown by the corresponding IR absorption at 2062 cm^{-1}. This reaction indicates that the coordination of dpa at the ruthenium centre occurs through the phosphorus atom rather than the C≡CH group.

No definite product was obtained from the reaction of complexes **1** with $NaPF_6$ in methanol in spite of the fact that cleavage of one Ru–Cl bond is known to occur under these conditions. Such a cleavage is involved in the formation of **3** in the presence of an excess of SMe_2 (eq. 4):

$$(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)Cl_2RuP(Ph_2)C{\equiv}CH + SMe_2 + NaPF_6 \xrightarrow{MeOH}$$

$$\left[(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)Ru(P(Ph_2)C{\equiv}CH)(Cl)(SMe_2)\right]^+ (PF_6)^- + NaCl \quad (4)$$

(3)



Scheme 1

Complex **3** was obtained in 75% yield as orange crystals after crystallization from dichloromethane–diethyl ether. No further transformation of complex **3**, involving the acetylenic function, was observed, contrasting with the reactivity of terminal alkynes towards $[(\eta^6\text{-arene})(SR_2)(L)RuCl]^+$ derivatives [4].

Stirring an equimolar mixture of **1a** and $(C_6Me_6)(PMe_3)RuCl_2$ in methanol in the presence of NH_4PF_6 (or $NaPF_6$) produced an orange precipitate that gave crystals upon addition of diethyl ether to its dichloromethane solution or upon slow evaporation of a methanol solution. The ^1H and ^{31}P NMR spectra revealed in the presence of two complexes in a molar ratio of about 10:1, and remained unchanged even after several attempts at separation. Both complexes appear from their NMR spectra to be dinuclear complexes resulting from the formation of a novel bridging phosphinocarbene group $Ph_2PCH_2(MeO)C$:, and are assumed to be two stereoisomers of **4** (Scheme 1).

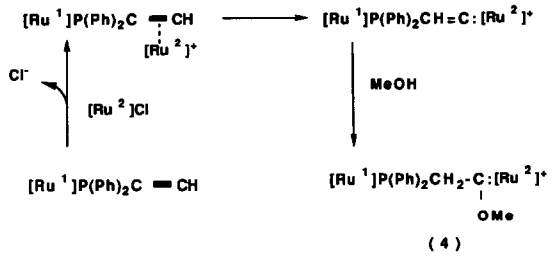
The identities of complexes **4** are based on the elemental analyses and NMR spectra. The ^1H NMR spectrum of the major isomer of **4** shows, in addition to the signals from the two arene ligands, a singlet at $\delta = 4.48$ ppm ($\delta = 4.06$ ppm for the minor isomer) attributable to a methoxy group. The bridging methylene CH_2P group appears as an ABX system. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at $\delta = 23.3$ and 6.0 ppm, with a $^4J(PP)$ coupling constant of 10 Hz, corresponding respectively to the PPh_2 and PMe_3 ^{31}P nuclei (assigned from the ^{31}P spectrum) coordinated to the two different ruthenium sites. The $^{13}C\{^1H\}$ NMR spectrum (Table 3) shows the carbenic carbon nucleus at $\delta = 317.1$ ppm coupled with the two phosphorus nuclei. For comparison, the ^{13}C NMR spectrum of

Table 3

$^{13}C\{^1H\}$ NMR [a] data for complexes **3** and **4**

Complex	Arene ligands	Other ligands
3	112.6, d, CMe, $J(PC) = 2.1$ Hz	133.3–128.5, m, Ph
	88.9, d, CH, $J(PC) = 3.3$ Hz	103.3, d, ≡CH, $^2J(PC) = 12.1$ Hz
	18.8, s, CH_3	77.2, d, PC≡, $^1J(PC) = 90$ Hz
		23.9, s, SMe_2
4	107.0, s, $C_6(Me_6)$	317.1, dd, CRu
		$^2J(PC) = 20.4$ Hz and 10.2 Hz
	95.6–83.4, m, $C_6(H_4)$	
	30.5, s, $CH(^iPr)$	136.1–129.1, m, Ph
	22.9, s, $CH_3(^iPr)$	69.1, s, OCH_3
	19.9, s, $CH_3(^iPr)$	56.1, dd, CH_2
		$^1J(PC) = 12.0$ Hz, $^3J(PC) = 7.6$ Hz
	17.5, s, $CH_3(C_6H_4)$	
	16.4, s, $CH_3(C_6Me_6)$	17.1, d, PMe_3, $^1J(PC) = 35.4$ Hz

[a] In CD_2Cl_2, 75.469 MHz, 297 K.



Scheme 2

$[C_6Me_6Ru{=}C(OMe)CH_2Ph(Cl)(PMe_3)](PF_6)$ shows a Ru=C signal at $\delta = 323.0$ ppm, $^2J(PC) = 20.6$ Hz [5]. The ^{31}P resonances of the minor isomer of complex **4** are observed as singlets at lower chemical shifts, $\delta = 18.3$ and 0.9 ppm.

In view of the known activation of terminal alkynes by ruthenium(II) complexes into vinylidenes [5], the formation of the bifunctional bridge is likely to result from the initial formation of a phosphinovinylidene ligand followed by addition of methanol to the electrophilic vinylidene carbon atom (Scheme 2). Hindered rotation around the Ru=C bond may be responsible for the observation of two isomers.

The synthesis of **4** thus illustrates the potential of diphenylphosphinoacetylene for generation of a bifunctional bridging ligand via activation of the C≡CH group. This process requires initial coordination of the phosphorus atom, and will probably provide a route to new mixed binuclear complexes.

Experimental

All manipulation were performed under an inert atmosphere by Schlenk techniques. Solvents were dried by conventional methods. NMR spectra were recorded on Bruker WP80 and AM300 spectrometers and IR spectra were recorded as Nujol mulls on a Nicolet 205 FT spectrometer. Analyses were performed by the "Service de Microanalyse du CNRS", Vernaison, France. The starting materials $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = *p*-$MeC_6H_4CHMe_2$, C_6Me_6 [6], 1,3,5-$Me_3C_6H_3$ [7]) were prepared by published methods, from $RuCl_3 \cdot 3H_2O$ (Johnson-Matthey). $Ph_2PC{\equiv}CH$ was prepared as previously described [8].

*(1,3,5-$Me_3C_6H_3$)$Cl_2RuP(Ph_2)C{\equiv}CH$, **1a**.* A solution of 2.10 g (10 mmol) of $Ph_2PC{\equiv}CH$ in 30 ml of dichloromethane was added to a solution of 3.54 g (10.0 mmol) of (1,3,5-$Me_3C_6H_3$)$(SMe_2)RuCl_2$ [4] in 30 ml of the same solvent. The mixture was stirred for 1 h at room temperature. The resulting red precipitate was filtered off, washed twice with 50 ml of diethyl ether, and dried under vacuum. Yield: 3.77 g (75%). IR, $\nu(C{\equiv}C) = 2044$ cm^{-1}.

*(p-$MeC_6H_4CHMe_2$)$Cl_2RuP(Ph_2)C{\equiv}CH$, **1b**.* A mixture of 2.70 g (4.41 mmol) of $[(p\text{-}MeC_6H_4CHMe_2)Cl_2Ru]_2$ and 1.85 g (8.82 mmol) of $Ph_2PC{\equiv}CH$ in 30 ml of chloroform was stirred for 12 h at room temperature. The resulting red solution was filtered and the filtrate covered with 100 ml of diethyl ether. The slow diffusion of ether produced dark red crystals, which were collected by decantation of the solvent, washed with 30 ml of ether, and dried under vacuum. Yield: 3.92 g (86%). IR, $\nu(C{\equiv}C) = 2044$ cm^{-1}.

[(C_6Me_6)(PMe_3)ClRuP(Ph_2)C≡CH](PF_6), 2. A mixture of 0.41 g (1.0 mmol) of (C_6Me_6)(PMe_3)$RuCl_2$, 0.42 g (2.0 mmol, excess) of $Ph_2PC{\equiv}CH$ and 0.17 g (1.0 mmol) of $NaPF_6$ in 30 ml of dry methanol was stirred at room temperature for 12 h. The resulting yellow slurry was evaporated to dryness and the residue extracted with 30 ml of dichloromethane. The solution was filtered and the filtrate covered with 100 ml of diethyl ether. The resulting dark orange crystals were isolated by decantation, washed with 30 ml of ether, and dried under vacuum. Yield: 0.50 g (69%). IR, $\nu(C{\equiv}C) = 2062\ cm^{-1}$.

[(1,3,5-$Me_3C_6H_3$)(SMe_2)ClRuP(Ph_2)C≡CH](PF_6), 3. A solution of 1.06 g (2.11 mmol) of **1a**, 0.50 ml (6.80 mmol, excess) of SMe_2 and 0.35 g (2.15 mmol) of $NaPF_6$ in a mixture of 30 ml of methanol and 10 ml of dichloromethane was stirred for 2 days at room temperature then evaporated to dryness. The residue was extracted with 40 ml of dichloromethane and the extract was filtered and the orange filtrate covered with 120 ml of diethyl ether. The resulting red orange crystals were isolated by decantation, washed with 30 ml of ether, and dried under vacuum. Yield: 1.06 g (75%). IR, $\nu(C{\equiv}C) = 2058\ cm^{-1}$.

{(p-$MeC_6H_4CHMe_2$)Cl_2Ru[μ-P(Ph_2)CH_2C(OMe)]Ru(Cl)(PMe_3)(C_6Me_6)}(PF_6), 4. A solution of 0.82 g (2.0 mmol) of (C_6Me_6)(PMe_3)$RuCl_2$, 1.03 g (2.0 mmol) of **1b** and 0.35 g (2.2 mmol, excess) of NH_4PF_6 in 30 ml of methanol was stirred for 2 days at room temperature. Diethyl ether (60 ml) was added and the resulting orange precipitate filtered off, dried under vacuum, and extracted with 30 ml of dichloromethane. The extract was filtered and the orange filtrate covered with 130 ml of diethyl ether. The dark-orange crystals resulting from diffusion of ether were collected, washed with 30 ml of ether, and dried under vacuum. Yield: 0.80 g (37%).

References

1 A.J. Carty, S.E. Jacobson, R.T. Simpson and N.J. Taylor, J. Am. Chem. Soc., 97 (1975) 7254.
2 P. Robert, H. Le Bozec, P.H. Dixneuf, F. Harstock, N.J. Taylor and A.J. Carty, Organometallics, 1 (1982) 1148.
3 B. Guilbert, B. Demerseman, P.H. Dixneuf and C. Mealli, J. Chem. Soc., Chem. Commun., (1989) 1035.
4 M. Gaye, B. Demerseman and P.H. Dixneuf, J. Organomet. Chem., 411 (1991) 263.
5 K. Ouzzine, H. Le Bozec and P.H. Dixneuf, J. Organomet. Chem., 317 (1986) C25; and Organometallics, 10 (1991) 2768.
6 M.A. Bennett, T.N. Huang, T.W. Matheson and A.K. Smith, Inorg. Synth., 21 (1982) 74.
7 M.A. Bennett and J.P. Ennett, Organometallics, 3 (1984) 1365.
8 C. Charrier, W. Chodkiewicz and P. Cadiot, Bull. Soc. Chim. Fr., (1966) 1002.