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Reactions of cationic hydrido complexes $[Ru(CO)H(MeCN)_2(PPh_3)_2]A$ ($A = ClO_4$, PF_6) with alkynes. The crystal structure of $[Ru(CO)(MeOOCC{=}CHCOOMe)(MeCN)_2(PPh_3)_2]ClO_4$

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Abstract

Reactions of $[Ru(CO)H(MeCN)_2(PPh_3)_2]A$ with mono- and di-substituted acetylenes give the alkenyl derivatives $[Ru(CO)(RC{=}CHR')(MeCN)_2(PPh_3)_2]A$ ($A = ClO_4$, $R = H$; $R' = C_3H_7$, CMe_3, Ph, COOMe; $R = R' =$ COOMe; $A = PF_6$, $R = R' =$ Ph) resulting from a *cis*-insertion of the alkyne into the Ru–H bond. The reaction of the perchlorate complex with diphenylacetylene yields alkenyl chlororuthenium derivatives resulting from the unexpected reduction of the perchlorate anion to chloride.

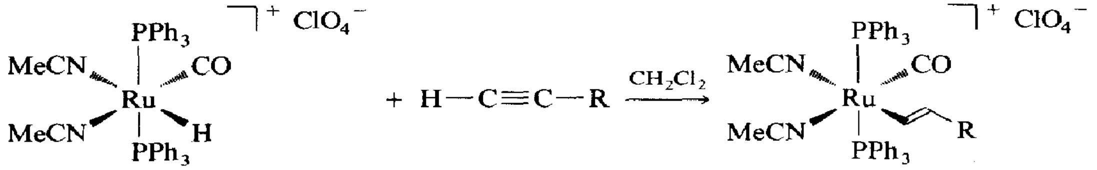
The crystal structure of $[Ru(CO)(MeOOCC{=}CHCOOMe)(MeCN)_2(PPh_3)_2]ClO_4$ has been determined by X-ray crystallography (orthorhombic, $P2_12_12_1$, *a* 14.498(1), *b* 15.080(1), *c* 22.677(2) Å). In this cationic complex both phosphine and acetonitrile molecules and, consequently, the carbonyl and alkenyl ligands are mutually *trans*, whereas in the other complexes only the phosphine ligands are in *trans* disposition, as inferred from ^1H NMR spectroscopic data.

Introduction

We previously reported on the reactions of neutral hydrido complexes $[Ru(CO)HCl(PR_3)_2L]$ ($L = PR_3$, Me_2Hpz; $R =$ Ph, p-$CH_3C_6H_4$) with alkynes [1–5], which generally gave alkenyl derivatives resulting from a *cis*-insertion of the alkyne into the Ru–H bond, although in a number of cases bis-insertion derivatives [3,5] or unexpected products [4,5] were obtained. We wish describe here a study of the reactions of the cationic hydrido complexes $[Ru(CO)H(MeCN)_2(PPh_3)_2]A$ ($A = ClO_4$, **1** [6]; $A = PF_6$, **2**) with mono- and di-substituted acetylenes $RC{\equiv}CR'$ ($R = H$; $R' = n\text{-}C_3H_7, CMe_3$, Ph, COOMe; $R = R' =$ COOMe, Ph)

Results and discussion

The reactions of cationic hydride **1** with monosubstituted acetylenes takes place readily in refluxing dichloromethane to give the *E*-alkenyl derivatives (**3**–**6**) in good yields (eq. 1). The *E* stereochemistry was assigned on the basis of the observed high values of the $^3J(^1H-^1H)$ coupling constants, and is consistent with a *cis*-insertion of the alkyne [1–5].



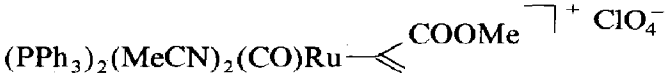
(**1**)

(**3**: $R = n\text{-}C_3H_7$;
4: $R = CMe_3$;
5: R = Ph;
6: R = COOMe)

(1)

The coordinated acetonitrile ligands in complexes **5** and **6** are judged to be in a *cis* disposition in the light of the appearance of two methyl signals in the high-field ^1H NMR spectra. The stereochemistry shown for complexes **3** and **4** should be regarded as tentative, since only a single resonance for the two acetonitrile ligands was observed in the ^1H NMR spectra.

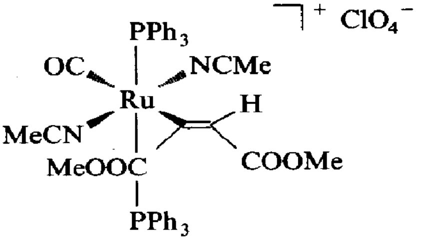
The reactions of neutral hydrides with methyl propiolate led to formation of bis-insertion products as a consequence of the high reactivity of this alkyne [3]. Reaction of **1** with one equivalent of methyl propiolate was monitored by ^1H NMR spectroscopy in deuterochloroform solution at 35 °C, and smooth formation of alkenyl complex **6** was observed. Kinetic evidence provided support for a rate-determining *cis*-insertion of hydride **1** with the alkyne to yield the hexa-coordinate complex **6** with an estimated second order rate constant $K_2 = 2.45 \times 10^{-2}\ M^{-1}\ s^{-1}$ (see Experimental section). Small amounts of secondary products appeared after longer reaction times. The major by-product (ca. 7%) exhibits two multiplets, at 4.38 and 5.73 ppm, characteristic of a $=CH_2$ group and two singlet resonances at 3.06 (3H) and 1.84 (6H) ppm for the methoxy group and two acetonitrile ligands, respectively. Thus, structure **7**, arising from an inverse addition, was assigned to this product.



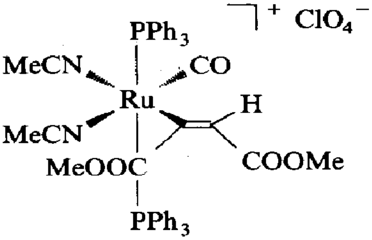
(**7**)

The reaction of the starting hydride **1** with dimethylacetylene dicarboxylate gave an equimolar ratio of two isomeric derivatives **8** and **9** in 70% yield. ^{1}H NMR spectroscopy indicated that consumption of **1** was complete after 60 h at 30 °C. Flash column chromatography [7] and crystallization afforded a pure sample of **8** in 26% yield. The ^{1}H NMR spectrum of this sample supports its formulation as insertion alkenyl derivative. The olefinic proton gives rise to a triplet ($^{3}J(^{1}H-^{31}P)$ 2.1 Hz) at 4.21 ppm and the acetonitrile ligands give rise to a singlet at 1.55 ppm Isomer **9** could not be isolated pure. Its ^{1}H NMR spectrum showed a multiplet at 4.77 ppm and two singlets at 1.77 and 1.66 ppm corresponding to mutually *cis*-acetonitrile ligands.

Noteworthy is the high (CO) frequency value of **8** (1990 cm^{-1}), which contrasts with the usual range 1950–1900 cm^{-1} for the alkenyl complexes **3**–**6**. This effect is probably related to the appearance of the olefinic proton at an unusual high field and is consistent with a relative *trans* coordination of the CO and alkenyl ligands, with the subsequent *trans* disposition of the ligands MeCN.

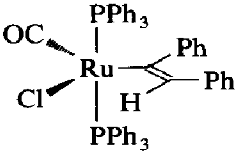


(8)



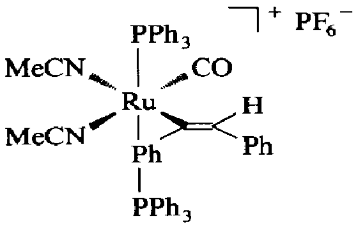
(9)

To our surprise, the reaction of hydride **1** with diphenylacetylene in refluxing dichloromethane gave a mixture of the known alkenyl complex **10** [1], and an acetonitrile complex [Ru(CO)Cl(PhC=CHPh)(MeCN)$(PPh_3)_2$] (**11**) (eq. 2).

1 + Ph—C≡C—Ph $\xrightarrow{CH_2Cl_2}$  + **11** (2)

(10)

The formation of **10** and **11** uncovers an unexpected reaction pathway for the perchlorate hydrido complex **1** triggered by the release of an acetonitrile ligand and subsequent formation of weakly coordinated perchlorate complex [8,9]. Reaction of cationic ruthenium hydride **2** with diphenylacetylene gave the expected insertion derivative **12** which contains two mutually *cis*-acetonitrile ligands. Further studies on the chemistry of other cationic ruthenium hydrides are in progress.



(12)

Description of the structure of compound 8

The structure of **8** consists of complex cations $[Ru(CO)(MeCN)_2(MeO_2CC{=}CHCO_2Me)(PPh_3)_2]^+$ and ClO_4^- anions. Selected bond lengths and angles are listed in Table 1. As can be seen from Fig. 1, the Ru atom displays a distorted octahedral coordination, with carbonyl, two nitrile ligands, and the alkenyl group in the equatorial plane, in which the two nitrile ligands are in *trans* positions. The two PPh_3 ligands are in the apical sites.

The atoms defining the equatorial plane (Ru, C1, C4, N1 and N2) are coplanar (largest deviation from the mean plane is 0.02(4) for N2). The two carboxylate groups (C2,C3,O2,O3) and (C5,C6,C7,O4,O5) are also planar, with largest deviations of 0.08(6) Å for C2 and 0.06(7) Å for C6 from their respective mean planes, which form angles of 87(2)° and 9(2)°, respectively, with the equatorial plane.

As expected from the difference in the π-acceptor characters of the carbonyl and alkenyl ligands, the Ru–C1 distance (1.86(5) Å) is significantly shorter than the Ru–C4 distance (2.12(5)Å).

No significant difference is observed between the two Ru–N distances (1.95(4) and 1.94(4) Å). The C4–C5 distance (1.41(7) Å), in the alkenyl group, appears to be longer than that observed in other alkenyl complexes, such as $[Ru(CO)Cl(PhC{=}CHPh)(PPh)_3)_2]$ (1.37(2) Å) [1], but this difference cannot be considered significant when account is taken of the estimated standard deviations.

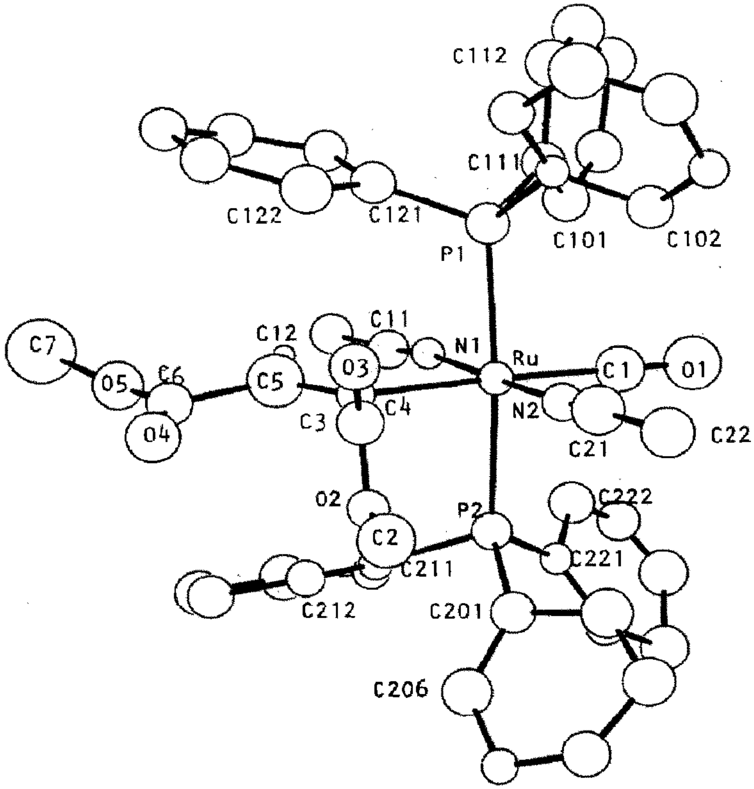


Fig. 1. ORTEP [14] drawing of the structure of the cationic species $[Ru(CO)(MeOOCC{=}CHCOOMe)(MeCN)_2(PPh_3)_2]^+$ (**8**) (atom numbering as in Tables 1 and 3). Numbering of the carbons of the phenyl rings omitted for clarity as are all the phenyl and methyl H atoms.

Table 1

Selected bond lengths (Å) and angles (deg) for compound 8 (esd's in parentheses).

Bond lengths [a]			
Ru–P1	2.37(1)	O2–C2	1.46(6)
Ru–P2	2.45(1)	C5–C6	1.58(8)
Ru–C1	1.86(5)	C6–O4	1.21(7)
Ru–N1	1.95(4)	C6–O5	1.26(7)
Ru–N2	1.94(4)	O5–C7	1.6(1)
Ru–C4	2.12(5)	C1–O1	1.16(6)
C4–C5	1.41(7)	N1–C11	1.17(6)
C4–C3	1.54(7)	C11–C12	1.57(8)
C3–O3	1.16(7)	N2–C21	1.03(7)
C3–O2	1.28(6)	C21–C22	1.68(9)
Bond angles [b]			
P1–Ru–P2	173.4(5)	Ru–C1–O1	172(5)
P1–Ru–C1	90(2)	Ru–N1–C11	174(4)
P1–Ru–N1	87(1)	N1–C11–C12	176(6)
P1–Ru–N2	91(1)	Ru–N2–C21	174(5)
P1–Ru–C4	89(1)	N2–C21–C22	168(6)
P2–Ru–C1	93(2)	Ru–C4–C3	117(3)
P2–Ru–N1	87(1)	Ru–C4–C5	122(4)
P2–Ru–N2	95(1)	O2–C3–O3	127(5)
P2–Ru–C4	89(1)	C4–C3–O3	121(5)
C1–Ru–N1	101(2)	C2–O2–C3	33(2)
C1–Ru–C4	170(2)	C4–C5–C6	127(5)
N1–Ru–N2	177(2)	C5–C6–O4	115(5)
N1–Ru–C4	89(2)	C5–C6–O5	105(5)
N2–Ru–C4	89(2)	C6–O5–C7	39(3)

[a] Mean P–C in Ph_3P ligands 1.81(6) Å; mean C–C in Ph rings 1.39(8) Å. [b] Mean C–C–C in Ph rings 120(5)°; mean Ru–P–C 116(2)°; mean C–P–C in PPh_3 ligands 102(3)°.

Experimental

IR spectra were recorded on a Pye Unicam SP spectrophotometer. Only the most significant IR frequencies for each new compound are given in the details of the preparations. ^{1}H NMR spectra were recorded on a Varian XL 300 (300 MHz) spectrometer with deuterochloroform solutions containing tetramethylsilane as internal standard.

Flash column chromatography [7] was performed on silica gel 60 (Macherey Nagel 230–400 mesh). Elemental analyses were performed with a Perkin–Elmer 240C Elemental Analyzer.

$[Ru(CO)H(MeCN)_2(PPh_3)_2]ClO_4$ (**1**) was prepared by a published procedure [6]. ^{1}H NMR δ 7.59–7.49 (m, 12H), 7.48–7.41 (m, 18H), 1.79 (s, 3H), 1.43 (s, 3H), −12.99(t, J 17.9 Hz, 1H).

$[Ru(CO)H(MeCN)_2(PPh_3)_2]PF_6$ (**2**) was prepared in the same way as **1** by use of $NaPF_6$. IR (KBr, cm^{-1}) 2320vw, 2290vw, 2050w, 1938vs, 840vs. ^{1}H NMR δ 7.57–7.45 (m, 30H), 1.72 (s, 3H), 1.34 (s, 3H), −13.00(t, J 17.7 Hz, 1H). Anal. Found: C, 55.55; H, 4.22; N, 3.16. $C_{41}H_{37}F_6N_2OP_3Ru$ calcd.: C, 55.85; H, 4.23, N, 3.18%.

$[Ru(CO)(HC{=}CHC_3H_7)(MeCN)_2(PPh_3)_2]ClO_4$ (**3**). A mixture of hydride **1** (109 mg, 0.13 mmol) and pent-1-yne (13 μl, 0.13 mmol) in CH_2Cl_2 (30 ml) was heated under reflux for 2 h. The yellow solution was evaporated, the residue was dissolved in 2 ml CH_2Cl_2, and the solution treated with Et_2O to give **3** as a beige solid (65 mg, 55%). IR (KBr, cm^{-1}) 2310vw, 2280vw, 1946vs, 1085vs. ^1H NMR δ 7.73–7.50(m, 12H), 7.50–7.30(m, 18H), 6.51 (dtt, J 15.6, 6.4, 1.1 Hz, 1H), 6.20 (dt, J 15.6, 1.5 Hz, 1H), 1.78 (m, 2H), 1.63 (s, 6H), 1.00 (sextet, J 7.2 Hz, 2H), 0.65 (t, J 7.2 Hz, 3H). Anal. Found: C, 60.91; H, 5.04; N, 3.11. $C_{46}H_{45}ClN_2O_5P_2Ru$ calcd.: C, 61.09; H, 5.02; N, 3.10%.

$[Ru(CO)(HC{=}CHCMe_3)(MeCN)_2(PPh_3)_2]ClO_4$ (**4**). A mixture of hydride **1** (111 mg, 0.13 mmol) and 3,3-dimethylbut-1-yne (17 μl, 0.13 mmol) in CH_2Cl_2 (30 ml) was heated under reflux for 1.5 h. The yellow solution was evaporated, the residue was dissolved in 2 ml CH_2Cl_2, and the solution treated with pentane to give **4** as a beige solid (82 mg, 67%). IR (KBr, cm^{-1}) 2280vw, 1900vs, 1092vs. ^1H NMR δ 7.56–7.52 (m, 12H), 7.50–7.40 (m,18H), 6.20 (dt, J 16.4, 0.8 Hz, 1H), 4.57 (d, J 16.4 Hz, 1H), 1.61 (s, 6H), 0.65 (s, 9H). Anal. Found: C, 61.28; H, 5.20; N, 3.04. $C_{47}H_{47}ClN_2O_5P_2Ru$ calcd.: C, 61.47; H, 5.16; N, 3.05%.

$[Ru(CO)(HC{=}CHPh)(MeCN)_2(PPh_3)_2]ClO_4$ (**5**). A mixture of hydride **1** (110 mg, 0.13 mmol) and phenylacetylene (15 μl, 0.13 mmol) in CH_2Cl_2 (30 ml) was heated under reflux for 2 h. The yellow-orange solution was concentrated to a volume of 2 ml and treated with pentane to afford **5** as an orange solid (83 mg, 67%). IR (KBr, cm^{-1}) 2300vw, 2285vw, 1950vs, 1545w, 1085vs. ^1H NMR δ 7.52–7.46 (m, 13H), 7.41–7.38 (m, 18H), 7.15 (t, J 7.5 Hz, 2H), 7.00 (t, J 7.3 Hz, 1H), 6.77 (d, J 7.3 Hz, 2H), 5.52 (d, J 17.0 Hz, 1H), 1.73 (s, 3H), 1.72(t, J 1.3 Hz, 3H). Anal. Found: C, 62.54; H, 4.63; N, 3.00. $C_{49}H_{43}ClN_2O_5P_2Ru$ calcd.: C, 62.73; H, 4.62; N, 2.99%.

$[Ru(CO)(HC{=}CHCOOMe)(MeCN)_2(PPh_3)_2]ClO_4$ (**6**). A mixture of hydride **1** (120 mg, 0.14 mmol) and methyl propiolate (13 μl, 0.14 mmol) was heated under reflux for 1.5 h in CH_2Cl_2 (30 ml). The yellow solution was evaporated and the residue was triturated with Et_2O to yield **6** as a yellow powder (72.5 mg, 55%). IR (KBr, cm^{-1}) 2300vw, 2280w, 1950vs, 1670s, 1535m, 1085vs. ^1H NMR δ 9.13 (dt, J 16.9, 1.9 Hz, 1H), 7.44–7.41 (m, 30H), 5.07 (dt, J 16.9, 1.3 Hz, 1H), 3.54 (s, 3H), 1.74 (s, 3H), 1.73 (t, J 1.3 Hz, 3H). Anal. Found: C, 58.59; H, 4.51; N, 3.05. $C_{45}H_{41}ClN_2O_7P_2Ru$ calcd.: C, 58.73; H, 4.49; N, 3.04.

Kinetic data for the reaction were recorded at 35 °C in a 5 mm NMR tube by monitoring the methoxyl signals of the crude reaction mixture. The rate constant was obtained by plotting 1/[methyl propiolate] against time ($R = 0.994$). The following rate law was found:

$$v = \frac{\mathrm{d[methyl\ propiolate]}}{\mathrm{d}t} = k[\text{hydride } \mathbf{1}][\text{methyl propiolate}]$$

The value of the second-order rate constant, k, was 2.45×10^{-2} M^{-1} s^{-1}.

$[Ru(CO)(MeOOC{=}CHCOOMe)(MeCN)_2(PPh_3)_2]ClO_4$ (*trans*-dinitrile isomer (**8**) + *cis*-dinitrile isomer (**9**)). A mixture of hydride **1** (172 mg, 0.14 mmol) and dimethyl acetylenedicarboxylate (30 μl, 0.24 mmol) in CH_2Cl_2 (10 ml) was stirred for 63 h at 23 °C. The resulting greenish-yellow solution was evaporated, the residue was dissolved in CH_2Cl_2 (5 ml), and the solution treated with hexane to afford a 1/1 mixture of **8** and **9** (140 mg, 70%). Flash column chromatography (10/1 EtOAc/

Table 2

Crystal analysis parameters for compound **8**

Formula	$[Ru(CO)(MeO_2CC{=}CHCO_2Me)(MeCN)_2(PPh_3)_2]ClO_4$ $C_{47}H_{43}ClN_2O_9P_2Ru$
Crystal habit	pale green prisms
Crystal size (mm)	$0.10 \times 0.08 \times 0.07$
Unit cell dimensions	14.498(1), 15.080(1), 22.677(2)Å
Symmetry	orthorhombic, $P2_12_12_1$
Packing: V(Å^3), Z	4957.9(7), 4
D(calcd)(g cm^{-3}), M, F(0,0,0)	1.3107, 978.33, 2008
μ(cm^{-1})	41.69
Experimental data	
Technique	four-circle diffractometer Philips PW 1100 monochromated Cu-K_α, θ_{max} 60°
No. of reflections	
measured	4139
independent	4109
observed	2023 ($I \leqslant 3\sigma(I)$ criterion)
standard reflections	400 and $\bar{4}$00 reflections every 90 min variation no
Solution and refinement	
solution	Patterson and Fourier synthesis
refinement	least-squares on F_0
absorption correction	yes,max and min 1.3840 and 0.7943, respectively; mean 1.010
Parameters	
no. of variables	249
degrees of freedom	1774
ratio of freedom	7.1
H atoms	calculated positions
Computer and programs	VAX 11/750, X RAY 80 System [10], DIRDIF [11], DIFABS [12], PARST [13], ORTEP [14]
Scattering factors	ref. 15
Anomalous dispersion	ref. 15
Final R	14.8%

EtOH) and crystallization (5/1 pentane/CH_2Cl_2) gave pure **8** as pale green crystals adequate for an X-ray structure determination (52 mg, 26%). **8**: IR (KBr, cm^{-1}) 1990vs, 1700vs, 1585m, 1568m, 1090vs. ^{1}H NMR δ 7.54–7.46 (m, 12H), 7.45–7.40 (m, 18H), 4.21 (t, J 2.1 Hz, 1H), 3.55 (s, 3H), 3.07 (s, 3H), 1.55 (s, 6H). **9**: ^{1}H NMR (as a 1/1 mixture with **8**) δ 7.60–7.40 (m, 30H), 4.77 (m, 1H), 3.56 (s, 3H), 3.05 (s, 3H), 1.77 (s, 3H), 1.66 (s, 3H). **8** + **9**: Anal. Found: C, 57.54; H, 4.45; N, 2.84. $C_{47}H_{43}ClN_2O_9P_2Ru$ calcd.: C, 57.68; H, 4.43; N, 2.86%.

Insertion reactions with diphenylacetylene. A mixture of hydride **1** (166 mg, 0.2 mmol) and diphenylacetylene (69 mg, 0.4 mmol) in 1,2-dichloroethane (10 ml) was heated under reflux for 24 h. The solvent was evaporated to yield $Ru(CO)Cl(PhC{=}CHPh)(PPh_3)_2$ (**10**), spectroscopically (^{1}H NMR and IR) identical with a sample prepared by reaction of diphenylacetylene with $Ru(CO)ClH(PPh_3)_3$ [1]. When the insertion reaction was carried out in CH_2Cl_2 at the reflux temperature

Table 3

Atomic parameters for all non-hydrogen atoms of [Ru(CO)(MeOOCC=CHCOOMe)(MeCN)$_2$(PPh$_3$)$_2$]ClO$_4$ [a]

Atom	x	y	z	U_{eq},Å^2
RU	0.3556(3)	0.5245(2)	−0.0117(2)	268(8)
CL	−0.5433(16)	−0.0725(16)	0.1081(10)	928(64)
P 1	0.2933(9)	0.4956(9)	0.0839(6)	383(36)
P 2	0.4086(9)	0.5407(9)	−0.1146(6)	371(34)
C 1	0.3059(35)	0.6409(34)	−0.0090(25)	436(134)
O 1	0.2778(31)	0.7090(30)	−0.0150(22)	805(136)
N 1	0.2529(27)	0.4572(26)	−0.0414(17)	349(103)
C 10	0.1966(36)	0.4106(33)	−0.0643(22)	306(125)
C 11	0.1221(46)	0.3513(43)	−0.0954(28)	688(194)
N 2	0.4678(25)	0.5887(24)	0.0235(16)	231(91)
C 20	0.5250(46)	0.6200(43)	0.0452(28)	609(182)
C 21	0.6057(78)	0.6750(70)	0.0672(47)	1422(401)
C 2	0.6788(45)	0.4513(45)	−0.0032(31)	832(227)
O 2	0.5873(23)	0.4320(22)	−0.0276(14)	380(90)
C 3	0.5330(33)	0.4099(33)	0.0139(26)	424(123)
O 3	0.5517(26)	0.4051(26)	0.0664(17)	487(105)
C 4	0.4305(34)	0.4023(33)	−0.0057(24)	416(132)
C 5	0.3907(33)	0.3200(33)	−0.0232(23)	404(133)
C 6	0.4407(41)	0.2294(39)	−0.0241(26)	521(161)
O 4	0.5248(28)	0.2310(27)	−0.0190(20)	676(120)
O 5	0.3811(30)	0.1729(28)	−0.0389(18)	681(134)
C 7	0.4212(60)	0.0749(59)	−0.0470(36)	954(282)
C101	0.3572(38)	0.5491(29)	0.1459(20)	349(114)
C102	0.3783(34)	0.6388(34)	0.1418(23)	362(134)
C103	0.4245(36)	0.6734(33)	0.1869(23)	355(131)
C104	0.4474(44)	0.6350(44)	0.2386(29)	611(182)
C105	0.4222(50)	0.5535(48)	0.2438(31)	778(217)
C106	0.3819(35)	0.5046(35)	0.1922(23)	524(157)
C111	0.1688(36)	0.5361(39)	0.0964(24)	515(157)
C112	0.1212(38)	0.5668(36)	0.0519(24)	430(153)
C113	0.0307(47)	0.6004(45)	0.0591(29)	617(190)
C114	0.0046(54)	0.5928(52)	0.1172(34)	816(228)
C115	0.0517(55)	0.5482(51)	0.1700(33)	865(246)
C116	0.1420(55)	0.5292(50)	0.1559(29)	800(187)
C121	0.2866(35)	0.3874(34)	0.1011(23)	352(128)
C122	0.3603(42)	0.3302(33)	0.1154(23)	428(131)
C123	0.3535(44)	0.2403(34)	0.1275(23)	463(134)
C124	0.2784(42)	0.1896(40)	0.1233(26)	518(163)
C125	0.2027(51)	0.2403(47)	0.0996(31)	740(208)
C126	0.2025(37)	0.3297(35)	0.0940(23)	428(140)
C201	0.5220(32)	0.5716(32)	−0.1288(20)	299(116)
C202	0.5469(51)	0.6579(49)	−0.1040(32)	794(221)
C203	0.6365(45)	0.6994(36)	−0.1090(24)	498(144)
C204	0.6967(56)	0.6502(56)	−0.1429(35)	881(249)
C205	0.6820(33)	0.5751(34)	−0.1706(21)	325(123)
C206	0.5887(34)	0.5383(35)	−0.1615(21)	379(128)
C211	0.3958(34)	0.4337(32)	−0.1574(21)	301(122)
C212	0.4653(35)	0.3721(34)	−0.1438(22)	357(130)
C213	0.4512(44)	0.2781(42)	−0.1756(28)	599(177)
C214	0.3790(44)	0.2696(42)	−0.2188(28)	586(192)
C215	0.3191(36)	0.3424(36)	−0.2236(23)	371(137)
C216	0.3279(34)	0.4191(35)	−0.1966(23)	395(137)

Table 3 (continued)

Atom	x	y	z	U_{eq},Å^2
C221	0.3380(47)	0.6106(43)	−0.1626(29)	646(188)
C222	0.2415(38)	0.6188(37)	−0.1570(24)	426(141)
C223	0.1814(36)	0.6767(35)	−0.1844(23)	371(135)
C224	0.2165(60)	0.7254(56)	−0.2065(37)	925(260)
C225	0.3024(52)	0.7296(48)	−0.2333(32)	737(216)
C226	0.3781(35)	0.6765(35)	−0.1990(24)	420(144)
O 6	−0.4560(41)	−0.0686(39)	0.0884(24)	1086(194)
O 7	−0.5726(53)	−0.1408(51)	0.0749(32)	1535(270)
O 8	−0.6051(77)	−0.0361(75)	0.0897(44)	2484(473)
O 9	−0.5501(45)	−0.0975(44)	0.1679(29)	1273(233)

[a] $U_{eq} = 1/3 |\Sigma(U_{ij} a_i^* a_j^* a_i a_j \cos(a_i, a_j))| \times 10^4$

for 16 h, a mixture of **10** and a major alkenyl derivative **11** was obtained. **11**: ^{1}H NMR δ 7.43–7.25 (m, 30H), 7.06 (m, 1H), 6.94–6.83 (m, 5H), 6.45 (d, J 7.3 Hz, 2H), 6.09 (d, J 7.3 Hz, 2H), 5.96 (br s, 1H), 1.41 (s, 3H).

A similar reaction was carried out with **2** as starting hydride. A mixture of **2** (123 mg, 0.15 mmol) and diphenylacetylene (27 mg, 0.15 mmol) in CH_2Cl_2 (15 ml) was heated under reflux for 22 h. The solvent was evaporated and the yellow solid was washed several times with Et_2O to yield, as a pale yellow powder, $[Ru(CO)(PhC{=}CHPh)(MeCN)_2(PPh_3)_2]PF_6$ (**12**) (50 mg, 32%). IR (KBr, cm^{-1}) 2280vw, 1950vs, 842vs. ^{1}H NMR δ 7.65–7.43 (m, 30 H), 7.02–6.90 (m, 3H), 6.78–6.54 (m, 3H), 6.42 (d, J 7.8 Hz, 2H), 6.22 (s, 1H), 6.16 (d, J 7.8Hz, 2H), 1.46 (s, 3H), 1.41 (s, 3H). Anal. Found: C, 62.35; H, 4.50; N, 2.66. $C_{55}H_{47}F_6N_2OP_3Ru$ calcd.: C, 62.32; H, 4.47; N, 2.64%.

*X-ray diffraction data for compound **8***

Table 2 gives the crystal analysis parameters of compound **8**. Table 3 gives the final atomic coordinates and thermal parameters for all non-hydrogen atoms of this compound.

Structure solution. Crystal data and structure solution conditions are summarized in Table 2. The skeleton of the complex cation was readily recognized in the Fourier synthesis. However, a poor convergence was obtained in the least-squares refinement. The anisotropic refinement leads to non-positive definite thermal parameters for some atoms, probably owing to the small size of the crystals. Thus the structure was refined only isotropically, allowing recognition of the chemical features. The ClO_4^- anions showed a very irregular geometry which could be not improved during the refinement. Lists of structure factors and thermal parameters are available from the authors.

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