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Methoxycarbene and Allenylidene Complexes of Ruthenium with an Oxygen Tripod Ligand

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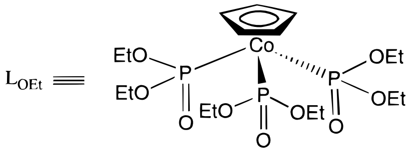
Summary: Interaction of $L_{OEt}(PPh_3)_2RuCl$ *(*L_{OEt} = $(\eta^5\text{-}C_5H_5)Co\{P(OEt)_2{=}O\}_3$*) with* $Me_3SiC{\equiv}CH$ *and 2-phenyl-3-butyn-2-ol in the presence of* NH_4PF_6 *in MeOH/THF afforded the structurally characterized methoxycarbene* $[L_{OEt}(PPh_3)_2Ru{=}C(OMe)Me]PF_6$ *(**1**) and the allenylidene complex* $[L_{OEt}(PPh_3)_2Ru{=}C{=}C{=}CPhMe]PF_6$ *(**2**), respectively. The Ru−C distances in **1** and **2** are 1.876(6) and 1.86(2) Å, respectively. The cyclic voltammograms of **1** and **2** exhibit reversible Ru(III/II) couples at 0.58 and 0.64 V vs* $Cp_2Fe^{+/0}$*, respectively.*

Introduction

Organometallic compounds supported by oxygen ligands are less common than the conventional organometallic compounds that are usually associated with soft hydrocarbyl ligands, notably carbonyl and cycloolefins. Kläui pioneered the synthesis of organometallic complexes with π-donating oxygen tripod ligands L_{OR} $[CpCo\{P(OR)_2{=}O\}_3]$, which may be considered as the oxygen analogues of cyclopentadienyl.[1] The ruthenium and rhodium complexes of L_{OR} were found to be catalysts for the oxidation of hydrocarbons[1] and alcohols[2] and hydrogenation of olefins.[3] Of particular interest are the organoruthenium complexes supported by oxygen ligands, which are relevant to the active species of Ru-mediated aqueous organometallic catalysis.[4] Recently, we found that the $L_{OEt}Ru$ fragment is considerably more basic than the CpRu congener and is capable of stabilizing a variety of π-acid ligands such as vinylidenes, olefins, and cyclic carbenes.[5] In our continuing effort to develop new metal catalysts with oxygen ligands, we describe the synthesis and molecular structures of the methoxycarbene and allenylidene complexes of ruthenium with L_{OEt}.

Experimental Section

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a



Bruker ALX 300 spectrometer operating at 300, 75, and 121.5 MHz for ^1H, ^{13}C, and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $Si(CH_3)_4$ (^1H and ^{13}C) and H_3PO_4 (^{31}P). Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 273A potentiostat. The working and reference electrodes were glassy carbon and $Ag/AgNO_3$ (0.1 M in acetonitrile), respectively. Potentials are reported with reference to $Cp_2Fe^{+/0}$. Elemental analyses were performed by Medac Ltd, Surrey, U.K.

Materials. NaL_{OEt}[6] and $L_{OEt}(PPh_3)_2RuCl$[5] were prepared according to the literature methods. $Me_3SiC{\equiv}CH$ and 2-phenyl-3-butyn-2-ol were purchased from Aldrich and used as received.

Synthesis of $\mathbf{[L_{OEt}(Ph_3P)_2Ru{=}C(OMe)Me]PF_6}$ **(1).** To a solution of $L_{OEt}(PPh_3)_2RuCl$ (70 mg, 0.06 mmol) and NH_4PF_6 (22 mg) in THF/MeOH (20 mL, 1:4) was added $Me_3SiC{\equiv}CH$ (0.1 mL), and the reaction mixture was stirred at room temperature for 1 day, during which the color changed from orange to yellow. The volatiles were removed and the residue was recrystallized from THF/hexane to give X-ray quality yellow crystals (yield 43 mg, 52%). ^1H NMR($CDCl_3$): δ 0.88 (t, 6H, CH_3), 1.12 (t, 6H, CH_3), 1.42 (t, 6H, CH_3), 3.11 (s, 3H, $Ru{=}C(CH_3)$), 3.31 (s, 3H, $Ru{=}C(OCH_3)$), 2.97−3.14 (m, 4H, OCH_2), 3.58−3.74 (m, 4H, OCH_2), 4.18−4.23 (m, 4H, CH_2), 5.01 (s, 5H, C_5H_5), 7.08−7.49 (m, 30H, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.9−16.4 (s, CH_3), 36.2 ($=CCH_3$), 59.7−61.5 (s, overlapping, $=CCH_3$ and OCH_2), 89.0 (s, C_5H_5), 127.1−134.8 (m, PPh_3), 311.9 (t, $^2J_{CP}$ = 14.4 Hz, $Ru{=}C$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −145.0 (PF_6), 45.8 (s, PPh_3), 106.3−107.9 (m, $PO(OEt)_2$). Anal. Calcd for $CoRuC_{56}H_{71}F_6O_{10}P_6$: C, 49.3; H, 5.2. Found: C, 49.1; H, 5.3.

Synthesis of $\mathbf{[L_{OEt}(Ph_3P)_2Ru{=}C{=}C{=}CMePh]PF_6}$ **(2).** To a solution of $L_{OEt}(PPh_3)_2RuCl$ (65 mg, 0.054 mmol) and NH_4PF_6 (20 mg), in THF/MeOH (30 mL, 1:4) was added 2-phenyl-3-butyn-2-ol (20 mg), and the reaction mixture was stirred at room temperature for 1 day. The volatiles were removed, and the residue was recrystallized from CH_2Cl_2/hexane to give X-ray quality red crystals (yield 43 mg, 55%). ^1H NMR ($CDCl_3$): δ 0.95 (t, 6H, CH_3), 1.08 (t, 6H, CH_3), 1.24 (t, 6H, CH_3), 1.83 (s, 3H, $=C(CH_3)$), 3.06−3.17 (m, 4H, OCH_2), 3.82−3.87 (m, 8H, OCH_2), 4.98 (s, 5H, C_5H_5), 7.04−7.94 (m, 35H, phenyl protons). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.9−16.3 (s, CH_3), 31.6 (s, $=CCH_3$), 61.1−61.5 (s, overlapping, OCH_2), 89.1 (s, C_5H_5), 127.1−140 (m, Ph), 151.8 (s, $Ru{=}C{=}C$), 220.7 (s,

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Table 1. Crystallographic Data and Experimental Details for [$L_{OEt}(PPh_3)_2Ru{=}C(OMe)Me]PF_6$ (1) and [$L_{OEt}(PPh_3)_2Ru{=}C{=}C{=}CMePh]PF_6$ (2)

	1	**2**
empirical formula	$CoRuC_{56}H_{71}F_6O_{10}P_6$	$CoRuC_{63}H_{73}F_6O_9P_6$
fw	1364.01	1434.10
color, habit	yellow, block	yellow, block
cryst dimens, mm	0.12 × 0.17 × 0.24	0.21 × 0.22 × 0.31
a, Å	14.201(1)	13.331(1)
b, Å	18.256(1)	21.128(2)
c, Å	23.880(1)	23.614(2)
β, deg	91.40(2)	
V, Å^3	6189.1(5)	6651.1(8)
Z	4	4
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$ (No 14)	$P2_12_12_1$ (No 19)
D_{calc}, g cm^{-3}	1.464	1.432
T, °C	25	25
λ, Å	0.710 73	0.710 73
scan type	ω	ω
$2\theta_{max}$, deg	51.2	49.4
μ, cm^{-1}	7.39	6.91
no. of reflns measd	30 618	19 741
no. of reflns obsd	5432	2128
weighting scheme	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
R,[a] %	4.57	6.1
R_w,[b] %	4.55	5.4
F(000)	2808	2952
GoF[c]	1.84	2.39

[a] $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [(\Sigma w^2|F_o| - |F_c|)^2/\Sigma w^2|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma w|F_o| - |F_c|)^2/(N_{obs} - N_{param}]^{1/2}$.

Ru=C=C=*C*), 311.8 (t, $^2J_{CP}$ = 26.4 Hz, Ru=*C*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −145.0 (PF_6), 40.6 (s, PPh_3), 109.5.3−110.2 (m, PO(OEt)$_2$). IR (Nujol, cm^{-1}): 1932 ($\delta_{C\equiv C}$). MS (FAB): *m/z* 1288 (M − PF_6)$^+$, 1026 (M − PF_6 − PPh_3)$^+$. Anal. Calcd for $CoRuC_{63}H_{73}F_6O_9P_6$: C, 52.8; H, 5.1. Found: C, 52.6; H, 5.2.

X-ray Diffraction Measurements. A summary of the crystallographic data and experimental details is given in Table 1. All data were collected on a MAR-Research image plate diffractometer at 25 °C. The structures for **1** and **2** were solved by heavy-atom Patterson and direct methods, respectively. All data were corrected for Lorentz and polarization and absorption effects with interimage scaling. The structures were refined by full-matrix least-squares analyses. For **1**, the positions of all non-hydrogen atoms were refined with anisotropic parameters, while for **2**, the positions of the non-hydrogen atoms were refined with either isotropic or anisotropic parameters. Hydrogen atoms were placed at the idealized positions (C−H = 0.95 Å). All calculations were performed using the teXan[7] crystallographic software package. Selected bond lengths and angles for **1** and **2** are listed in Tables 2 and 3, respectively. Atomic coordinates are given in the Supporting Information.

Results and Discussion

Syntheses and Crystal Structures. Reaction of $L_{OEt}(PPh_3)_2RuCl$ with $Me_3SiC{\equiv}CH$ in the presence of NH_4PF_6 afforded the methoxycarbene complex [$L_{OEt}(PPh_3)_2Ru{=}C(OMe)Me]PF_6$ (**1**), isolated as air-stable yellow crystals. The carbene is presumably formed via nucleophilic attack of MeOH on the unisolated vinylidene intermediate [$L_{OEt}(PPh_3)_2Ru{=}C{=}CH_2]PF_6$. Apparently, the unsubstituted vinylidene complex [$L_{OEt}(PPh_3)_2Ru{=}C{=}CH_2]^+$ is more susceptible to nucleophilic attack than the substituted analogue, such as [$L_{OEt}(PPh_3)_2Ru{=}C{=}CHPh]^+$, which was found to be unreactive toward alcohols under the same conditions.[5] It may be noted that reaction of $Cp(PPh_3)_2RuCl$ (Cp = η^5-C_5H_5) with $Me_3SiC{\equiv}CH$ in CH_2Cl_2 or MeOH afforded [$Cp(PPh_3)_2Ru{=}C{=}CH_2]^{+}$ [8] or [$Cp(PPh_3)_2Ru{=}C(OMe)Me]^+$,[9] respectively. Figure 1 shows the structure of the cation [$L_{OEt}(PPh_3)_2Ru{=}C(OMe)Me]^+$; selected bond lengths and angles are listed in Table 2. As expected, the carbene moiety in **1** lies in the idealized symmetry plane of the molecule and the plane of carbene fragment

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [$L_{OEt}(Ph_3P)_2Ru{=}C(OMe)Me]PF_6$ (1)

Ru(1)−P(4)	2.335(1)	Ru(1)−P(5)	2.330(2)
Ru(1)−O(1)	2.153(4)	Ru(1)−O(4)	2.179(3)
Ru(1)−O(7)	2.247(4)	Ru(1)−C(18)	1.876(6)
O(10)−C(18)	1.343(6)	O(10)−C(20)	1.447(8)
C(18)−C(19)	1.849(9)		

P(1)−Ru(1)−P(5)	98.15(5)	P(4)−Ru(1)−O(1)	87.02(10)
P(4)−Ru(1)−O(4)	170.4(1)	P(4)−Ru(1)−O(7)	96.66(10)
P(4)−Ru(1)−C(18)	90.5(2)	P(5)−Ru(1)−O(1)	174.45(10)
P(5)−Ru(1)−O(4)	90.8(1)	P(5)−Ru(1)−O(7)	95.7(1)
P(5)−Ru(1)−C(18)	87.2(2)	O(1)−Ru(1)−O(4)	83.7(1)
O(1)−Ru(1)−O(7)	83.1(1)	O(1)−Ru(1)−C(18)	93.3(2)
O(4)−Ru(1)−O(7)	79.9(1)	O(4)−Ru(1)−C(18)	92.4(2)
O(7)−Ru(1)−C(18)	171.8(2)	Ru(1)−C(18)−O(10)	122.6(4)
Ru(1)−C(18)−C(19)	122.8(4)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [$L_{OEt}(Ph_3P)_2Ru{=}C{=}C{=}CMePh]PF_6$ (2)

Ru(1)−P(4)	2.3392(1)	Ru(1)−P(5)	2.3291(1)
Ru(1)−O(1)	2.16(1)	Ru(1)−O(4)	2.17(1)
Ru(1)−O(7)	2.13(1)	Ru(1)−C(18)	1.86(2)
C(18)−C(19)	1.23(2)	C(19)−C(20)	1.37(3)

P(4)−Ru(1)−P(5)	99.369(4)	P(4)−Ru(1)−O(1)	85.5(3)
P(4)−Ru(1)−O(4)	92.9(3)	P(4)−Ru(1)−O(7)	173.4(3)
P(4)−Ru(1)−C(18)	90.5(5)	P(5)−Ru(1)−O(1)	175.1(3)
P(5)−Ru(1)−O(4)	99.2(3)	P(5)−Ru(1)−O(7)	85.8(3)
P(5)−Ru(1)−C(18)	90.0(6)	O(1)−Ru(1)−O(4)	80.8(4)
O(1)−Ru(1)−O(7)	89.3(4)	O(1)−Ru(1)−C(18)	89.6(6)
O(4)−Ru(1)−O(7)	82.2(4)	O(4)−Ru(1)−C(18)	169.5(6)
O(7)−Ru(1)−C(18)	93.6(6)	Ru(1)−C(18)−C(19)	169(1)
C(18)−C(19)−C(20)	177(2)	C(19)−C(20)−C(21)	117(2)
C(19)−C(20)−C(22)	121(2)		

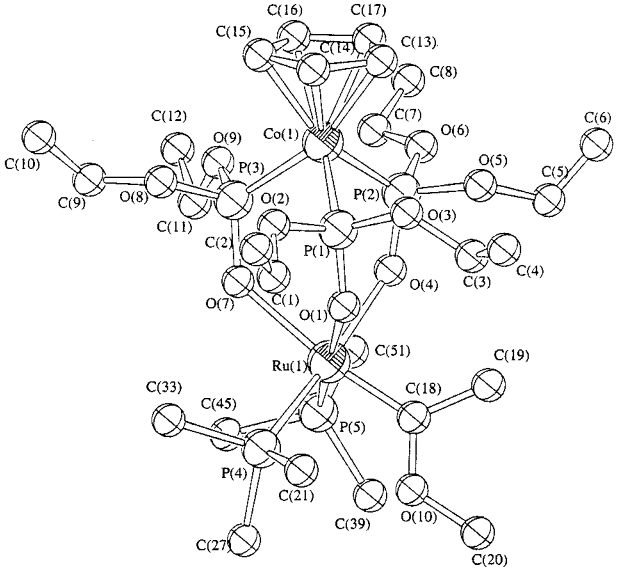

Figure 1. Perspective view of the cation [$L_{OEt}(PPh_3)_2Ru{=}C(OMe)Me]^+$. The phenyl rings of PPh_3 are omitted for clarity.

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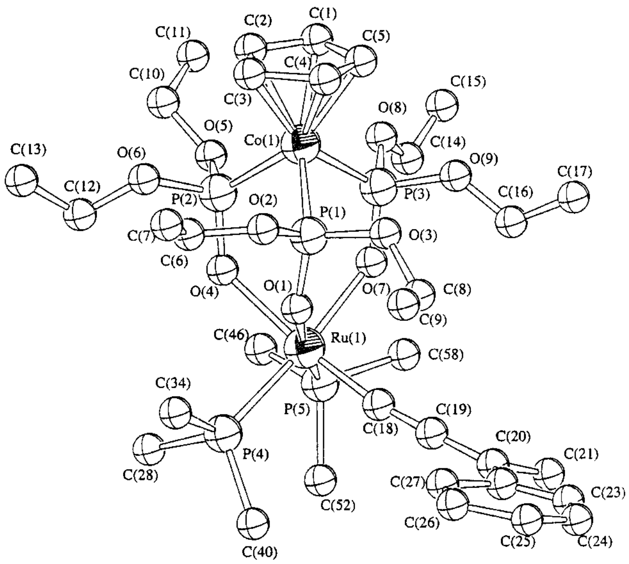
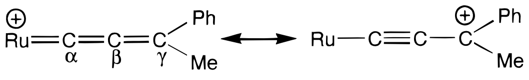


Figure 2. Perspective view of the cation $[L_{OEt}(PPh_3)_2\text{-}Ru{=}C{=}C{=}CPhMe]^+$. The phenyl rings of PPh_3 are omitted for clarity.

bisects the P−Ru−P angle. The Ru−C distance of 1.876(6) Å is slightly shorter than that for the cyclopentadienyl analogue $[Cp(PPh_3)_2Ru{=}C(OMe)Et]^+$ (1.959(6) Å)[10] and similar to that for the cyclic carbene complex $[L_{OEt}(PPh_3)_2Ru{=}\overline{C(CH_2)_3O}]^+$ (1.87(1) Å).[5] The Ru−O(trans to C) distance is long (2.247(4) Å), apparently due to the strong trans influence of the carbene ligand. The ^{13}C NMR spectrum of **1** shows a triplet at δ 311 ($^2J_{CP}$ = 14.4 Hz) assignable to the carbenic carbon.

Similarly, treatment of $L_{OEt}(PPh_3)_2RuCl$ with 2-phenyl-3-butyn-2-ol afforded the allenylidene complex $[L_{OEt}(PPh_3)_2Ru{=}C{=}C{=}CMePh]PF_6$ (**2**), isolated as air-stable red crystals. Figure 2 shows a perspective view of the cation $[L_{OEt}(PPh_3)_2Ru{=}C{=}C{=}CMePh]^+$; selected bond lengths and angles are given in Table 3. As anticipated, the linear allenylidene fragment (C(α)−C(β)-C(γ) = 177(2)°) lies in the idealized symmetry plane of the molecule. The Ru−C(α) distance of 1.86(2) Å is comparable to that in $[Cp(PMe_3)_2Ru{=}C{=}C{=}CPh_2]^+$ (1.884(5) Å).[11] The C(α)−C(β), C(α)−C(γ) distances of 1.23(2) and 1.37(3) Å, respectively, are indicative of a significant contribution of the resonance form **II** for the allenylidene moiety.

Accordingly, the IR spectrum of **2** displays a strong absorption at 1932 cm^{-1}, assignable to $\nu_{C\equiv C}$. The ^{13}C chemical shift for the C(α) was found at δ 311.8, which is higher than that for $[Cp(PMe_3)_2Ru{=}C{=}C{=}CPh_2]^+$ (δ 295.8).[11] The resonant signals for C(β) and C(γ) were observed at δ 220.7 and 151.8, respectively.



I **II**

Electrochemistry. The cyclic voltammograms for complexes **1** and **2** in CH_2Cl_2 show reversible oxidation couples at 0.58 and 0.64 V vs $Cp_2Fe^{+/0}$, respectively. $[L_{OEt}(PPh_3)_2Ru{=}C{=}CHPh]^+$ and $[L_{OEt}(PPh_3)_2RuCO]^+$, which was synthesized from $[L_{OEt}(PPh_3)(CO)Ru(OH_2)]^+$ [5] and PPh_3, exhibit irreversible oxidation waves at similar potentials (0.62 and 0.75 V, respectively), suggesting that the π acidity of carbene, vinylidene, and allenylidene is comparable to that of carbonyl. We tentatively assign these oxidation processes as the metal-centered oxidations. This assignment is in agreement with the extended-Hückel molecular-orbital calculation by Kirchner and co-workers on the analogous nitrogen tripod system $[Tp(tmen)Ru{=}C{=}CHPh]^+$ (Tp = hydridotris(pyrazolyl)borate, tmen = *N,N,N′,N′*-tetramethylethylenediamine), the HOMO of which is believed to be mainly the dπ(Ru) orbitals.[12] However, the assignment of the ruthenium oxidation state in the vinylidene and carbene complexes is not unambiguous. Although Kirchner and co-workers formulated $[Tp(tmen)Ru{=}C{=}CHPh]^+$ as a Ru(IV) complex, we favor the formulation of Ru(II) for $[L_{OEt}(PPh_3)_2RuX]^+$ (*X* = carbene, vinylidene, and allenylidene) on the basis of the X-ray structural data. For example, the average Ru−O distances in **1** and **2** (2.193 and 2.15 Å, respectively) are closer to that in $L_{OEt}(PPh_3)_2Ru^{II}Cl$ (2.182 Å) than to that in tetravalent $[L_{OEt}(H_2O)Ru^{IV}]_2(\mu\text{-}O)_2$ (2.051 Å).[3] Accordingly, the oxidation of complexes **1** and **2** at 0.58 and 0.64 V is assigned as the respective Ru(III/II) couple.

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Supporting Information Available: Tables of calculated atomic coordinates, bond lengths and angles, and thermal parameters for **1** and **2** (25 pages). Ordering information is given on any current masthead page.

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