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Synthesis and Characterization of η⁶-Arene Ruthenium Complexes Bearing Oxopentadienyl and Phosphine Ligands

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Dedicated to Professor Heinrich Nöth on the Occasion of His 85th Birthday

Keywords: Arenes; Oxopentadienyl; Phosphines; Ruthenium

Abstract. An addition reaction of dinuclear $[(\eta^6\text{-}C_6Me_6)Ru(\eta^{3,1}\text{-}exo\text{-}syn\text{-}CH_2CHCHCHO)]_2(BF_4)_2$ (**1**) with different Lewis bases in acetone results in the formation of mononuclear $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}exo\text{-}syn\text{-}CH_2CHCHCHO)(L)](BF_4)$ (L = PMe_3, **2**; PPh_3, **3**; $PHPh_2$, **4**; Ph_2PEtPy, **6**; CO, **7**) and dinuclear $[\{(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}exo\text{-}syn\text{-}CH_2CHCHCHO)\}_2(\mu_2\text{-dppe})](BF_4)_2$ (**5**). The addition of $Ph_2PCH_2CH_2PPh_2$ to the dinuclear product **1** affords **5** which show a bridging phosphine between two ruthenium centers. A comparative study of the new cationic arene derivatives and the corresponding isoelectronic Cp*Ru(heteropentadienyl) is established. All compounds were characterized by IR spectroscopy, high resolution mass spectrometry, NMR spectroscopy and the crystal structures of **2** and **3** are also described.

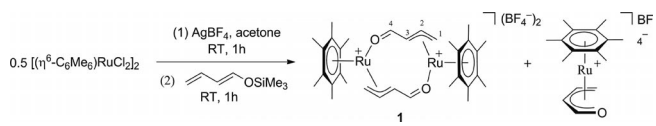
Dedicated Cluster

Introduction

Because of the interesting chemistry displayed by the half-open ruthenocene complexes with oxopentadienyl ligands,[1] and their major differences relative to the pentadienyl complexes,[1,2] raises considerable interest in the chemistry of the isoelectronic cationic $(\eta^6\text{-arene})Ru^{II}$(heteropentadienyl) analogues.[3]

Previous results showed that there is a greater competition among alternative bonding modes for the (η^6-arene)Ru(heteropentadienyl) derivatives compare to the Cp*Ru(heteropentadienyl) analogues. In fact, a mixture of η^5- and $\eta^{3,1}$-oxopentadienyl compounds $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}CH_2CHCHCHO)]BF_4$ and $[(\eta^6\text{-}C_6Me_6)Ru(\eta^{3,1}\text{-}exo\text{-}syn\text{-}CH_2CHCHCHO)]_2(BF_4)_2$ (**1**) was obtained from the reaction of 1-trimethylsilyloxy-1,3-butadiene and $[(\eta^6\text{-}C_6Me_6)Ru(acetone)_3](BF_4)_2$, where the dinuclear oxopentadienyl product **1** has been the first structurally characterized example of a complex bearing a bridging oxopentadienyl ligand,[3] Scheme 1.

In this report, we described the study of the reactivity of the dicationic complex **1** towards addition reactions, and the contrastingly results upon addition of Lewis bases to the isoelectronic neutral Cp*Ru(η^5-oxopentadienyl) derivatives.



Scheme 1. Synthesis of the mixture of **1** and $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}CH_2CHCHCHO)]BF_4$.

Additionally, it has also been reported that reactions of arenes with organometallic species to form η^6-arene ruthenium compounds have been found numerous applications in organic synthesis[4] and as chemical entities of biological interest.[5]

Results and Discussion

Synthesis and Spectroscopic Characterization of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^{3,1}\text{-}exo\text{-syn-}CH_2CHCHCHO)(L)](BF_4)$ (L = PMe_3, **2**; PPh_3, **3**; $PHPh_2$, **4**; 2-(2-diphenylphosphinoethyl) pyridine (Ph_2PEtPy), **6**; CO, **7**) and $[\{(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}exo\text{-syn-}CH_2CHCHCHO)\}_2(\mu_2\text{-dppe})](BF_4)_2$ (**5**)

The new compounds **2**–**7** were prepared by addition of Lewis bases, such as PPh_3, PMe_3, $PHPh_2$, dppe, Ph_2PEtPy and CO, by thermal reactions (**2**–**6**), and at room temperature (**7**), as described in Scheme 2. Compounds **2**–**7** are yellow solids, air-stable in solid state and slightly sensitive in solution. All compounds are soluble in acetone, nitromethane, acetonitrile and chlorinated solvents, and insoluble in diethyl ether, ethanol and hydrocarbons. Compound **6** reacts in chlorinated solvents to afford compound $(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}CH_2CHCHCHO)Cl$ (**8**).[3] Several attempts to improve the synthetic procedure for obtaining **6** were unsuccessful, and there was no evidence of coordination of the pyridine molecule to the ruthenium atom.

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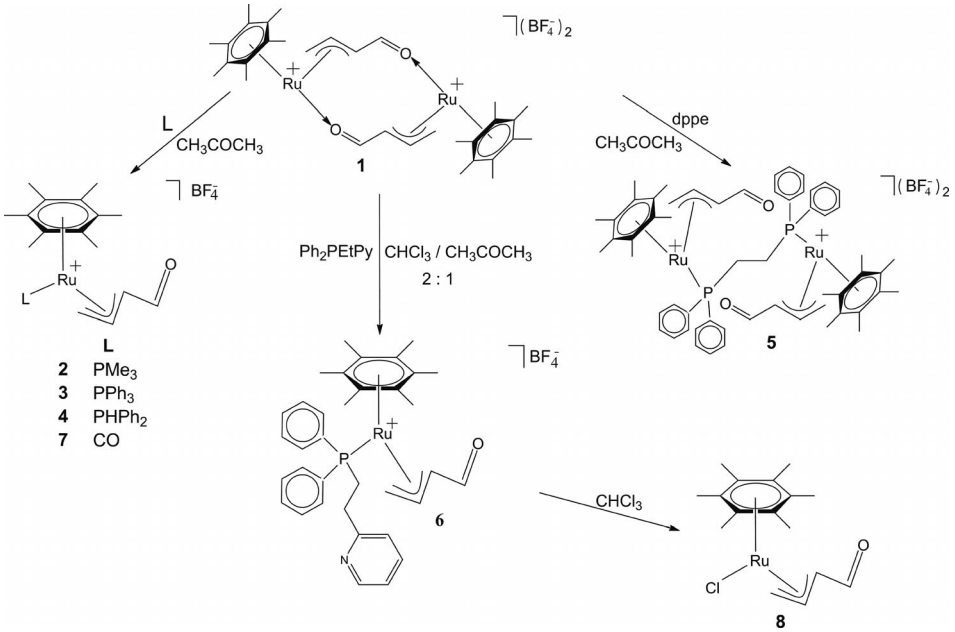

Scheme 2. Synthesis of compounds **1–8**.

A similar P-coordination neutral complex [(η⁶-C_6Me_6)Ru(κ¹-*P*-$PPh_2EtPy)Cl_2$] has been reported from reaction of the dimer [(η⁶-C_6Me_6)$RuCl_2]_2$ and PPh_2EtPy.[6] Also, the P,N-chelated cationic complex [(η⁶-C_6Me_6)Ru(κ²-*P*-N-PPh_2EtPy)Cl]PF_6 has been isolated.[6]

IR spectra of compounds **2–6** show evidence of an uncoordinated C=O group of the oxopentadienyl ligand (1665–1674 cm^{-1}, KBr). The IR spectrum of **7** revealed the presence of the carbonyl group of the oxopentadienyl ligand at 1675 cm^{-1} and the metal-carbonyl ligand at 2034 cm^{-1}.

The $^{31}P\{^1H\}$ NMR spectra of compounds **2–4** and **6** show a single singlet resonance at 5.9, 50.7, 34.9 and 39.0 ppm, respectively; while the spectrum of compound **5** shows a doublet at 41.5 with J = 14.9 Hz, which indicates the inequivalence of the two phosphorus nuclei of the bidentate ligand in a spectral region typical of non-chelating phosphines. During monitoring of the formation of **5** through the $^{31}P\{^1H\}$ NMR spectra, after 1.5 h, under mild heating acetone, two phosphorus signals are observed as doublets at 41.8 and –10.5 ppm with J_{PP} = 34.7 Hz, another doublet at δ = 41.5 ppm with J_{PP} = 14.8 Hz, and free dppe. These three resonances are observed in 1.0:0.6:0.4 ratio, and after 2h they change to 0.3:1.0:0.0 ratio, which indicates the presence of both κ¹- and μ²- coordination modes for the dppe ligand: an intermediate species **5′**, where one end of the dppe ligand is not coordinated to the metal atom (δ = –10.5 ppm) and another end which is coordinated to ruthenium (δ = 41.8 ppm) and the final product **5** with the bridging ligand (δ = 41.5 ppm). Finally, after 3 h there is evidence of total conversion to **5**. The same results were obtained after monitoring the reaction at room temperature, but longer times were required, see Supporting Information. A similar ^{31}P NMR spectroscopic behavior has been reported for compounds [{(η⁶-*p*-cymene)$RuClN_3$}$_2$(μ$_2$-dppe)] [δ = 26.7 (d)],[7a] [{(η⁶-C_6Me_6)$RuXN_3$}$_2$(μ$_2$-dppe)] [X = N_3, δ = 31.1],[7b] [X = Cl, δ = 30.3],[7b] [(η⁶-C_6H_6)$RuCl_2]_2$(μ$_2$-dppe) [δ = 23.3 (s)],[7c] [{$CpRu(N_3)$}$_2$(μ$_2$-dppe)$_2$] [δ = 39.19],[8a] [{CpRuCl}$_2$(μ$_2$-dppe)$_2$] [δ = 37.10],[8a] and [{$CpRu(SnCl_3)_2$}$_2$(μ$_2$-dppe)] [δ = 43.5 (s)],[8b] as well as three intermediates species observed in the phosphine substitution reactions between $CpRuCl(PPh_3)_2$ and dppe: $CpRuCl(PPh_3)$(κ¹-dppe) [δ = 41.51 (d), –12.10],[8a] $CpRuCl(\kappa^1\text{-dppe})_2$ [δ = 40.72 (d), –12.31],[8a] and [{$CpRuCl(PPh_3)$}$_2$(μ$_2$-dppe)] [δ = 43.11 (d), 42.76 (d)].[8a] In agreement with the presence of a bridging dppe ligand in compound **5**, the ^{31}P NMR shows an upfield shift compared to complexes where the dppe is acting as a chelate in mononuclear ruthenium derivatives, such as: [(η⁶-C_6H_6)Ru(κ²-dppe)Cl]Cl [δ = 70.4 (s)],[7c] $CpRuCl(\kappa^2\text{-dppe})$ [δ = 79.9],[9] [$CpRu(L)(\kappa^2\text{-dppe})]BPh_4$ [δ = 78.3–82.9],[9] Cp*$RuX(\kappa^2$-dppe) [X = Cl, δ = 73.5–74.6],[10,11] [X = N_3, δ = 75.7],[11] [X = H, δ = 90.2],[12] [Cp*$RuX(\kappa^2\text{-dppe})]BF_4$ [X = $(H)_2$, δ = 71.3, (η^2-H_2), δ = 77.4],[12] and $CpRu(\kappa^2\text{-dppe})SnCl_3$ [δ = 77.8 (s)],[8b] or dinuclear compounds where the bidentate dppe is also coordinated only to one metal atom, such as {$Cp(PPh_3)_2Ru$}C≡C-C≡C{$Ru(\kappa^2$-dppe)Cp} δ = 86.1 and {$Cp(\kappa^2\text{-dppe})_2Ru$}C≡C-C≡C{$Ru(\kappa^2$-dppe)Cp} δ = 86.7 ppm.[13]

The ^1H and ^{13}C NMR spectroscopy of compounds **2–7** gave evidence of the η³-*exo-syn*-oxodienyl coordination to the metal center, as well as the expected η⁶-C_6Me_6 ligand. The chemical shifts are quite similar, and typical of those found for enyl moieties coordinated to ruthenium,[1,3] singlet signals at δ = 1.82–2.44 ppm are assigned to the hydrogen atoms of the hexamethylbenzene ligand, where the lower frequency is observed in **5**. ^1H NMR demonstrated that compound **7** and the neutral analogue Cp*Ru(η³-*exo-syn*-$CH_2C(Me)CHC(Me)O)CO$ have similar trends, showing higher frequency chemical shifts compare to those of the corresponding cationic and neutral phos-

phine derivatives. Compound **6** was only assigned by ^{1}H NMR spectroscopy.

High resolution mass spectrometry shows a parent ion corresponding to mononuclear structures for **2**–**4** and **6**. In the case of compounds **2**–**4** and **6**, the base peak correspond to the molecular ion, giving evidence of the stability of the monodentate phosphine derivatives, while **5** shows the fragment [(η^6-C_6Me_6)Ru(dppe)(C_4H_5O)]$^+$ and **7** easily loose CO to afford the base peak at 333 *m*/*z*. The peak signal at 333 is present in all compounds, which suggest that either (η^6-C_6Me_6)Ru(η^3-CH_2CHCH_2)(CO) or (η^6-C_6Me_6)Ru(η^3-$CH_2CHCHCHO$) fragments are favored. The former is proposed based on the easy decarbonylation observed in compound (η^6-C_6Me_6)Ru(η^5-$CH_2CHCHCHO$) affording the *exo* and *endo*-allylic derivatives (η^6-C_6Me_6)Ru(η^3-CH_2CHCH_2)(CO).[3]

Crystal Structures of 2 and 3

Perspective views of the molecular structures of compounds **2** and **3** are shown in Figure 1 and 2, respectively. Crystal data, experimental parameters, and selected bond and angles are given in Table 1 and 2, respectively.

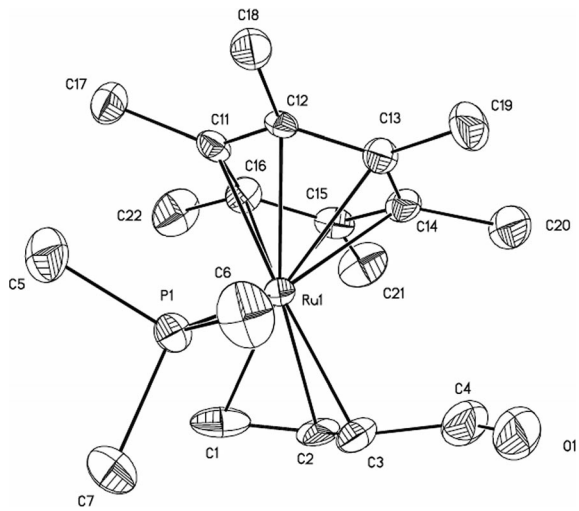

Figure 1. Molecular structure of **2**. (ORTEP plot, 45 % probabilities). Hydrogen atoms have been omitted for clarity.

X-ray crystallography confirmed the structures proposed for **2** and **3** on the basis of spectroscopic data. Compounds **2** and **3** are discrete cationic molecules where the oxodienyl ligand is very similar in the two complexes, with respective values for the Ru-oxopentadienyl fragment of Ru–C1 [2.215(10), 2.201(6) Å], Ru–C2 [2.124(8), 2.132(7) Å], Ru–C3 [2.222(8), 2.230(7) Å]. The latter is not significantly different from compounds with *exo* conformation with respect to the arene ligand in **1** [2.204(4), 2.142(4), 2.221(3) Å] and (η^6-C_6Me_6)Ru(η^3-*exo*-CH_2CHCH_2)(CO) [2.235(5), 2.150(5), 2.228(6) Å][3] and clearly different from characteristic d^4 configuration of the ruthenium atom,[14] as the neutral *endo* Ru^{IV} derivatives: Cp*Ru(η^3-*endo-syn*-$CH_2C(Me)CHC(Me)O)Cl_2$ [2.187(3), 2.196(3), 2.238(3) Å] and Cp*Ru(η^3-*endo-syn*-CH(Me)-$CHCHOEt)Cl_2$ [2.207(4), 2.172(4), 2.410(4) Å]. The C–C bond lengths within the enyl ligand show an asymmetrical bond to the metal atom [C1–C2 1.387(16), 1.394(11); C2–C3 1.425(14), 1.437(10) Å] in **2** and **3**, which can be compared to (η^6-arene)Ru(η^3-*exo-syn*-$CH_2C(Me)CHC(Me)O)Cl$ (arene = C_6H_6, C_6Me_6) [C1–C2 1.434(6), 1.417(4); C2–C3 1.411(5), 1.438(4) Å].[3] The C1–C2–C3 angle [118.7(10), 117.6(8)] is close to 120°, as typically observed in η^3-allyl ruthenium

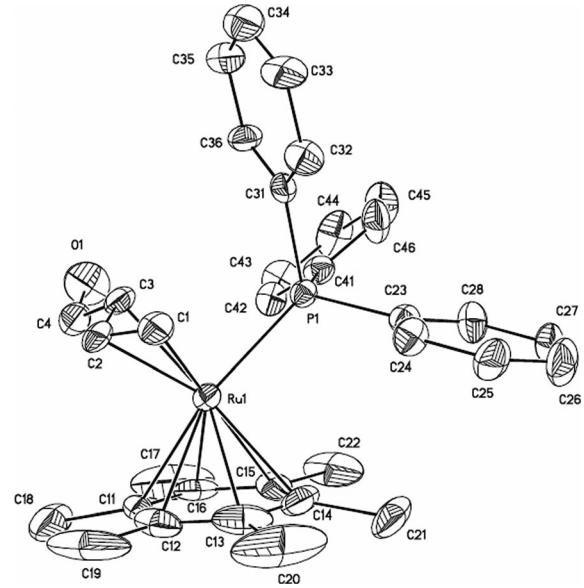

Figure 2. Molecular structure of **3**. (ORTEP plot, 45 % probabilities). Hydrogen atoms have been omitted for clarity.

Table 1. Crystal and structure refinement data for compounds **2** and **3**.

Compound	**2**	**3**
Empirical formula	$C_{19}H_{32}ORuPBF_4$	$C_{34}H_{39}ORuPBF_4$
Formula weight	495.30	682.50
Crystal system	Monoclinic	Othorrombic
Space group	*P*21	*Pna*21
Unit cell dimensions /Å, °	*a* = 9.2682(4) *b* = 8.9115(4) *c* = 13.1031(7) *β* = 97.92(2)°	*a* = 10.6876(2) *b* = 29.4988(2) *c* = 9.9956(6) *β* = 90°
V /Å^3	1071.91(9)	3151.3(2)
Z	2	4
Crystal size /mm	0.51 × 0.21 × 0.15	0.75 × 0.67 × 0.56
D_{calc} /g·cm^{-3}	1.535	1.439
F(000)	508	1404
Absor. coeff. /mm^{-1}	0.846	0.598
Absor. correction	Multi-Scan	Spherical
T /K	293(2)	293(2)
θ Range for data collection / deg	3.14 to 54.90	4.06 to 54.92
Index ranges	–12 ≤ *h* ≤ 5 –11 ≤ *k* ≤ 9 –16 ≤ *l* ≤ 16	–9 ≤ h ≤ 13 –28 ≤ k ≤ 38 –10 ≤ l ≤ 10
no. of reflns collcd	5765	12077
no. of indpt reflns	4073 (R_{int} = 0.0494)	5238 (R_{int} = 0.0274)
no. indpt obsd [$F > 4\sigma(F)$]	3035	4450
Final R_1 [$F > 4\sigma(F)$]	0.0598	0.0583
Final wR_2 [$F > 4\sigma(F)$]	0.1211	0.1094
GOF	1.035	1.260

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structures.[3,14–16] The long bond length for Ru–C4 [**3**, 3.0637(122); **4**, 3.1504(103) Å] and the corresponding short distance for C4–O1 [**3**, 1.222(13); **4**, 1.217(11) Å] confirmed the exclusive η³- coordination of the oxopentadienyl ligand.

The dihedral angles corresponding to the oxopentadienyl ligands in **2** and **3** show similar deviation from planarity [**2**, 7.22(1.08°); **3**, 6.14(0.89°)] and can be compared with (η⁶-arene)Ru(η³-$CH_2C(Me)CHC(Me)O)Cl$ [arene = C_6Me_6, 18.5(4°). C_6H_6, 1.3(6°)], where a greater and slight distortion is observed. The metal–arene bond lengths C–C reflect the expected higher steric demand of the methyl substituents in the hexamethylbenzene ligands, Table 2. Consistent with the crystallographically characterized Cp*Ru(η³-$CH_2C(Me)CHC(Me)O)PPh_3$, a longer bond Ru-PPh_3 is observed for the cationic oxopentadienyl complex **3** compare to the isoelectronic neutral complex.

Table 2. Selected bond lenghts /Å and angles /° for compounds **2** and **3**.

Compound	**2**	**3**
Bond lenghts		
C1–C2	1.387(16)	1.394(11)
C2–C3	1.425(14)	1.437(10)
C3–C4	1.422(13)	1.454(11)
C4–O1	1.222(13)	1.217(11)
Ru1–C1	2.215(10)	2.201(6)
Ru1–C2	2.124(8)	2.132(7)
Ru1–C3	2.222(8)	2.230(7)
Ru1–P1	2.3407(19)	2.362(2)
Ru1–C_6Me_6 (centroid)	1.783(10)	1.807(10)
Bond Angles		
C1–C2–C3	118.7(10)	117.6(8)
C2–C3–C4	121.9(10)	121.2(8)
C3–C4–O1	127.7(11)	121.8(9)
C1–Ru1–C2	37.2(4)	37.5(3)
C1–Ru1–C3	66.1(4)	66.3(4)
C2–Ru1–C3	38.2(4)	38.4(3)
C2–Ru1–C12	163.3(3)	91.4(3)
C3–Ru1–C11	174.8(3)	100.7(2)
C3–Ru1–C14	102.1(3)	167.6(3)
C1–Ru1–P1	87.0(4)	88.0(2)
C3–Ru1–P1	81.3(3)	84.6(2)
C11–Ru1–P1	97.91(14)	156.04(19)
C12–Ru1–P1	92.13(15)	154.4(2)
C15–Ru1–P1	162.10(14)	95.38(14)

A comparative investigation into the reactivity of the cationic arene derivatives **2**–**4** and the corresponding isoelectronic Cp*Ru(η³-$CH_2C(Me)CHC(Me)O)PR_3$ (R = Me, Ph or R_3 = $PHPh_2$) provides an important assessment of the electronic factors, which shows that the addition reactions proceed more selectively (**2**, 70 %; **3**, 79 %; **4**, 88 %) in the case of derivatives of **1**. Also strong Ru–P bond became evident in the isolated cationic complex **3**, whereas a facile dissociation of PPh_3, along with the consequent formation of Cp*Ru(η⁵-$CH_2C(Me)CHC(Me)O$), occurs in solution for the neutral complex Cp*Ru(η³-$CH_2C(Me)CHC(Me)O)PPh_3$.[1] The highest yield of all phosphine adducts Cp*Ru(η³-$CH_2C(Me)CHC(Me)O)PR_3$ was obtained for R = Me (70 %), likely due to the strong basicity and small size of PMe_3, while the PR_3 = $PHPh_2$ derivative, analogue to **4**, was always obtained in a mixture with Cp*Ru(η⁵-$CH_2C(Me)CHC(Me)O$). Compound **1** did not underwent addition reactions with nitrogen ligands, such as piperazine and the unsaturated 1,2-di-*tert*-butyl-(ethylenediamine).

Conclusions

As a result of this study, it is clear the preference of the phosphorus vs. nitrogen as ligands in cationic arene-oxopentadienyl derivatives. Once dimer **5** is formed, it does not tend to dissociate to yield the entropy-favored chelate monomer. The same behavior is observed in the cationic mononuclear complex **6**, where the nitrogen atom is not coordinated to the metal. It is apparent that the reactivity of **1** and their oxopentadienyl neutral analogues is strongly influenced by electronic properties of both the metal complex, and a more reactive bridging η³,¹-oxopentadienyl vs. η⁵-oxopentadienyl ligands. According to the time of reaction, the addition of different reactants to **1** shows the following trend: **2** > **3** > **4** > **5** > **7**, which are in agreement with the steric and electronic properties of the corresponding donor ligands.

Experimental Section

Synthetic work was carried out in a dry nitrogen atmosphere using standard Schlenk-techniques. All solvents were purified by conventional procedures and distilled under nitrogen prior to use. Deuterated solvents were degassed. The $RuCl_3 \cdot 3H_2O$ and phosphines were used as received from Pressure Chemicals, Sigma–Aldrich and Strem Chemicals, and CO was industrial grade. Compounds $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$,[17] $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$,[17] and **1**[3] were prepared by published methods.

The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker 300, Jeol GSX-270 and Jeol Eclipse 400 MHz instruments and referenced internally using the residual protio and carbon solvent resonances relative to tetramethylsilane. External standard for ^{31}P was H_3PO_4 (85 %). Assignment of ^1H and ^{13}C NMR signals are based on 1D and 2D spectra. High resolution mass spectra were obtained by LC/MSD TOF on an Agilent Technologies instrument with APCI as ionization source. Infrared spectra were recorded with a FT-IR Perkin–Elmer 1600 spectrometer using KBr pellets (4000–400 cm^{-1}). Melting points were determined in a Melt-Temp Gallenkamp (digital) and are uncorrected.

General Method for the Preparation of Compounds [(η⁶-C_6Me_6)Ru(η³-exo-syn-$CH_2CHCHCHO$)](L)(BF_4) (L = PMe_3, 2; PPh_3, 3; $PHPh_2$, 4; $Ph_2CH_2CH_2Ph_2$) and [{(η⁶-C_6Me_6)Ru(η³-exo-syn-$CH_2CHCHCHO$)}₂(μ₂-dppe)](BF_4)₂ (5)

A mixture of **1** (100 mg, 0.12 mmol) and the phosphine in acetone (20 mL) was heated in an oil bath until ^1H and ^{31}P NMR spectroscopic monitoring of the reaction mixture showed complete consumption of the starting material and no further change in the spectrum was observed. The reaction times were the following: **2**, 40 min; **3**, 70 min; **4**, 2.5 h; **5**, 3 h. After reach room temperature, the solution was filtered and the volume of the solvent was reduced to approx. 2 mL. Addition of diethyl ether afforded precipitation of yellow or yellow-orange sol-

ids, which were filtered and washed with diethyl ether (2 × 3 mL) and samples were dried under vacuum. All compounds melt with decomposition.

[(η⁶-C₆Me₆)Ru(η³-exo-syn-CH₂CHCHCHO)(PMe₃)] (BF₄) (2)

PMe_3 (27.0 μL, 0.26 mmol). Oil bath at 45 °C. The yellow-orange crystalline solid was obtained in 70% yield (82.0 mg, 0.17 mmol). M. p. 206–207 °C. **IR** (KBr): $\tilde{\nu}$ = 2982 cm^{-1} (s), 2920 (s), 2219 (w), 1947 (s, br), 1669 (vs), 1552 (m), 1433 (s), 1392 (s), 1296 (s), 1057 (vs, br), 957 (s), 854 (m), 728 (m), 676 (m), 622 (w), 520 (m), 456 (w) cm^{-1}. **ESI+TOF:** *m/z* 409.1229 error 0.0556 ppm; DBE 4.5. **2**: $C_{19}H_{32}BF_4OPRu$: C, 46.07; H, 6.51. Found: C, 46.34; H, 6.46. **^{31}P NMR** (CD_3NO_2): δ = 5.9 (s). **^{1}H NMR** (CD_3NO_2): δ = 1.79 (m, approx. 13.0, $H1_{anti}$), 2.78 (dd, 2.5, 10.0, $H1_{syn}$), 4.21 (m, 10.0, H2), 2.38 (m, overlapped, H3), 9.10 (d, 5.1, H4), 2.26 (s, C_6Me_6), 1.42 (d, 9.5, PMe_3).**^{13}C NMR** (CD_3NO_2): δ = 43.6 (t, 1.5, C1), 80.5 (d, 2.7, C2), 56.4 (s, ap, C3), 198.1 (d, 7.0, C4), 104.9 (s, C_6Me_6), 15.7 (s, overlapped, C_6Me_6), 15.7 (m, PMe_3).

[(η⁶-C₆Me₆)Ru(η³-exo-syn-CH₂CHCHCHO)(PPh₃)] (BF₄) (3)

PPh_3 (62.6 mg, 0.24 mmol). A pale yellow crystalline solid was obtained in 79% yield (128.7 mg, 0.19 mmol). M. p. 208–209 °C. **IR** (KBr): $\tilde{\nu}$ = 3027 cm^{-1} (w, br), 2000–1750 (w, br), 1665 (vs), 1483 (m), 1437 (s), 1390 (m), 1288 (w), 1057 (vs, br), 803 (w), 750 (s), 701(s), 621 (w), 529 (s), 488 (m), 422 (w) cm^{-1}. **ESI+TOF:** *m/z* 595.1700 error 0.2881 ppm; DBE 16.5. **^{31}P NMR** (CD_3NO_2): δ = 50.7 (s). **^{1}H NMR** (CD_3NO_2): δ = 1.87 (m, approx. 14.0, $H1_{anti}$), 3.06 (dd, 1.8, 7.2, $H1_{syn}$), 4.22 (m, 7.0, 10.1, H2), 2.29 (m, 7.0, 9.5, H3), 9.18 (d, 6.8, H4), 1.94 (s, C_6Me_6), 7.58 (br. s, PPh_3).**^{13}C NMR** (CD_3NO_2): δ = 43.9 (s, C1), 83.0 (s, C2), 58.0 (s, C3), 198.4 (s, C4), 106.0 (s, C_6Me_6), 15.2 (s, C_6Me_6), 135.0 (d, 9.6, *o*), 128.8 (d, 10.5, *m*), 131.4 (s, *p*), 130.0 (d, 31.5, *i*).

[(η⁶-C₆Me₆)Ru(η³-exo-syn-CH₂CHCHCHO)(PHPh₂)] (BF₄) (4)

$PHPh_2$ (10 wt.-% in hexane) (0.72 mL, 0.24 mmol). Oil bath at 52 °C. A canary-yellow solid was obtained in 88% yield (126.0 mg, 0.21 mmol). M. p. 214–215 °C. **IR** (KBr): $\tilde{\nu}$ = 3026 cm^{-1} (w, br), 2922 (w, br), 2851 (w, br), 2752 (vw), 2345 (m), 2000–1750 (w, br), 1670 (vs), 1585 (vw), 1542 (m), 1483 (m), 1439 (s), 1389 (m), 1320 (w), 1287 (w), 1190 (w, sh), 1137 (s, sh), 1059 (vs, br), 910 (m), 868 (s), 746 (s), 700(s), 622 (m), 511 (s), 477 (w), 438 (s) cm^{-1}. **ESI+TOF:** *m/z* 519.1385 error 0.0321 ppm; DBE 12.5. **4**: $C_{28}H_{34}BF_4OPRu$: C, 55.55; H, 5.66. Found: C, 55.25; H, 5.62. **^{31}P NMR** (CD_3NO_2): δ = 34.9 (s). **^{1}H NMR** (CD_3NO_2): δ = 1.52 (dd, approx. 12.0, $H1_{anti}$), 2.96 (d, 7.0, $H1_{syn}$), approx. 4.30 (overlapped, H2), 2.10–2.20 (overlapped, H3), 9.13 (d, 6.3, H4), 2.17 (s, C_6Me_6), 7.30–7.65 (m, PH*Ph*$_2$) 6.88 (d, approx. 370.0, PH). **^{1}H NMR** [$(CD_3)_2CO$]: δ = 1.45 (m, approx. 12.5, $H1_{anti}$), 3.02 (d, 6.7, $H1_{syn}$), 4.60 (m, 7.7, 9.5, H2), 2.21 (m, overlapped, H3), 9.22 (d, 6.2, H4), 2.21 (s, C_6Me_6), 7.09 (d, 374.1, Ph_2PH), 7.24–7.58 (m, PH*Ph*$_2$), 7.09 (d, 374.0, PH). **^{13}C NMR** [$(CD_3)_2CO$]: δ = 46.6 (s, C1), 83.6 (s, C2), 57.1 (s, C3), 197.2 (s, C4), 105.0 (s, C_6Me_6), 15.3 (s, C_6Me_6), 133.6 (d, 8.8, *o*), 134.1 (d, 9.7, *o*), 129.3 (d, ap, *m*), 129.4 (d, ap, *m*), 131.1 (s, *p*), 131.7 (s, *p*).

[{(η⁶-C₆Me₆)Ru(η³-exo-syn-CH₂CHCHCHO)}₂(μ₂-Ph₂CH₂CH₂Ph₂)](BF₄)₂ (5)

1,2-diphenylphosphinoethane (dppe) (57.0 mg, 0.14 mmol). Oil bath at 52 °C. A pale yellow solid was obtained in 52% yield (76 mg, 0.06 mmol). M. p. 185–187 °C. **IR** (KBr): $\tilde{\nu}$ = 3056 cm^{-1} (m, br), 3024 (m, br), 2928 (m), 2861 (w, sh), 1975 (w, br), 1674 (vs), 1610 (vw, sh), 1488 (m), 1439 (s), 1393 (m), 1288 (w), 1186 (vw, sh), 1057 (vs, br), 876 (w), 824 (w), 751 (m), 703 (s), 616 (w), 521 (s), 492 (w, sh), 449 (w) cm^{-1}. **ESI+TOF:** *m/z* 731.2071 [$(\eta^6$-$C_6Me_6)$Ru(dppe)-$(C_4H_5O)]^+$, 662.1741 [$(\eta^6$-$C_6Me_6)$Ru(dppe)$]^+$, 333.07547 [$(\eta^6$-$C_6Me_6)$Ru(dppe)(C_3H_5)(CO)$]^+$, 305.080297 [$(\eta^6$-$C_6Me_6)$Ru$(C_3H_5)]^+$. **5**: $C_{58}H_{70}B_2F_8O_2P_2Ru_2$: C, 56.32; H, 5.70. Found: C, 56.44; H, 5.57. **^{31}P NMR** (CD_3NO_2): δ = 41.5 (d, 14.9). **^{1}H NMR** (CD_3NO_2): δ = 1.81–1.85 (overlapped, $H1_{anti}$), 2.91 (d, 7.3, $H1_{syn}$), 4.18 (m, 7.4, 10.2, H2), 2.29 (m, H3), 9.11 (dd, 2.0, 6.1, H4), 1.82 (s, C_6Me_6), 7.36–7.72 (m, Ph_2, dppe), 1.88–2.08 (m, CH_2, dppe). **^{31}P NMR** [$(CD_3)_2CO$]: δ = 42.3 (d, 22.3). **^{1}H NMR** [$(CD_3)_2CO$]: δ = 1.88 (overlapped, $H1_{anti}$), 3.02 (d, ap, 7.2, $H1_{syn}$), 4.34 (m, 9.4, 13.0, H2), 2.30 (overlapped, H3), 9.23 (dd, 2.0, 5.7, H4), 1.88 (s, C_6Me_6), 7.40–7.95 (m, Ph_2, dppe), 1.70–2.00 (m, CH_2, dppe).**^{13}C NMR** [$(CD_3)_2CO$]: δ = 44.2 (s, C1), 82.3 (d, 7.7, C2), 56.8 (s, C3), 197.8 (d, 3.1, C4), 105.6 (s, C_6Me_6), 15.6 (s, C_6Me_6), 133.8 (m, *o*), 132.0 (m, *m*), 129.7 (s, *p*) 24.2 (br, CH_2). The intermediate species **5'** was detected through the monitoring the reaction of **5**: **^{31}P NMR** (CD_3NO_2): δ = 41.8 (d, 34.7), –10.5 (d, 37.2). **^{1}H NMR** (CD_3NO_2): δ = approx. 2.15 (m, $H1_{anti}$), 2.94 (dd, 1.9, 7.4, $H1_{syn}$), approx. 4.20 (m, 1.8, 7.0, 9.7 H2), 2.50 (m, H3), 9.14 (d, 6.1, H4), 1.92 (s, C_6Me_6), 7.30–7.70 (m, Ph_2, dppe), 2.07, 2.11 (s, CH_2, dppe), 1.70–2.40 (m, CH_2, dppe). **^{13}C NMR** (CD_3NO_2): δ = 43.7 (d, 4.6, C1), 82.4 (s, C2), 56.9 (s, C3), 198.3 (s, C4), 105.4 (s, C_6Me_6), 15.7 (s, C_6Me_6), [dppe: 133.4 (t, 8.5), 132.9 (d, 7.7), 132.7 (d, 7.7), 131.2 (s), 129.1 (d, 10.0), 128.3–128.8 (m), 25.6 (dd, 7.7, 24.6), 23.7 (dd, 6.2, 16.6)].

[(η⁶-C₆Me₆)Ru(η³-exo-syn-CH₂CHCHCHO)(Ph₂PEtPy)] (BF₄) (6)

A mixture of **1** (100 mg, 0.12 mmol) and 2-(2-diphenylphosphinoethyl)pyridine (Ph_2PEtPy) (34.7 mg, 0.12 mmol) was heated in refluxing chloroform/acetone (2:1) (20 mL). No further change was observed even after 4 h. The ^{1}H and ^{31}P NMR showed a mixture of **1**, **6** and the previously isolated (η^6-C_6Me_6)Ru(η^3-$CH_2CHCHCHO$)Cl (**8**).[3] The solution was filtered through Celite® 545 removing compound **1**. The volume of the remaining yellow solution was reduced to a minimum and a chromatographic column with desactivated alumina[18] and elution of dicholoromethane/acetone (1:1) gave 3 fractions, from the first orange band compound **8** as an orange powder was isolated in 15.3% (56.5 mg, 0.15 mmol), while in the second yellow band, **6** was isolated as yellow powder in 18.4% (27.6 mg, 0.04 mmol). Compound **6**: **ESI+TOF:** *m/z* 624.1964 error 0.0358 ppm; DBE 16.5. **^{31}P NMR** [$(CD_3)_2CO$]: δ = 39.0 (s). **^{1}H NMR** [$(CD_3)_2CO$]: δ = approx. 2.05 (overlapped, $H1_{anti}$), approx. 3.00 (overlapped, $H1_{syn}$), 4.39 (dd, 7.5, 9.9, H2), 2.47 (overlapped, H3), 9.30 (d, 6.1, H4), 2.50 (s, C_6Me_6), 7.10–7.35, 7.50–7.98 (m, Ph_2, Ph_2PEtPy), 2.90–3.20 (m, CH_2, Ph_2PEtPy), 8.58 (m, 4.8). Compound **8**: M. p. 182–185 °C (dec). **IR** (KBr): 3319 (w), 3066 (s), 2919 (s, br), 2802 (s), 2731 (s), 2269 (w), 2110 (w), 1940 (w), 1815 (w), 1666 (vs), 1490 (s), 1441 (s, br), 1390 (s, br), 1136 (s), 1007 (s, br), 907 (s) cm^{-1}. **ESI+TOF:** *m/z* 369.0553 error 0.4 ppm. **^{1}H NMR** ($CDCl_3$): δ = 2.66 (dd, 0.8, 11.3, $H1_{anti}$), 3.20 (d, 6.9, $H1_{syn}$), 4.49 (ddd, 7.1, 9.9, 11.3, H2), 3.40 (dd, 10.1, H3), 9.73 (d, 3.3, H4), 2.06 (s, C_6Me_6). **^{13}C NMR** ($CDCl_3$): δ = 56.7 (s, C1), 87.9 (s, C2), 66.0 (s, C3), 199.0 (s, C4), 97.8 (s, C_6Me_6), 15.5 (s, C_6Me_6).

[(η⁶-C₆Me₆)Ru(η³-exo-syn-CH₂CHCHCHO)(CO)] (BF₄) (7)

A solution of **1** (100 mg, 0.12 mmol) in acetone (20 mL) was placed in a glass reactor and CO was introduced at 1.5 bar. After stirring 16

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h, an amber suspension was observed; it was filtered and the lemon-yellow solution was evaporated under reduced pressure to yield a lemon-yellow solid in 76 % (86.0 mg, 0.19 mmol). M. p. 256–257 °C. **IR** (KBr): $\tilde{\nu}$ = 3433 cm^{-1} (m, br), 2999 (w, br), 2953 (w, br), 2862 (w, sh), 2346 (w, br), 2035 (vs), 1675 (vs), 1497 (m), 1451 (s), 1394 (s), 1294 (m), 1251 (w, sh), 1128 (vs, sh), 1128 (vs, sh), 1059 (vs), 881 (w, sh), 741 (m), 619 (w), 586 (w), 538 (m), 519 (m), 499 (s), 471 (m) cm^{-1}. **ESI+TOF:** *m/z* 361.0739 error 0.7225 ppm; DBE 6.5. **7**: $C_{17}H_{23}BF_4O_2Ru$: C, 45.65; H, 5.18. Found: C, 46.01; H, 4.99. **^{1}H NMR** (CD_3NO_2): δ = 2.70 (d, 10.0, $H1_{anti}$), 3.26 (dd, 1.8, 7.0, $H1_{syn}$), 4.64 (dddd, 5.9, 7.2, 10.2 H2), 3.11 (dd, 4.6, 10.0, H3), 9.32 (d, 4.5, H4), 2.44 (s, C_6Me_6). **^{13}C NMR** [$(CD_3)_2CO$]: δ = 46.6 (s, C1), 85.4 (s, C2), 56.9 (s, C3), 195.8 (s, C4), 111.3 (s, C_6Me_6), 16.0 (s, overlapped, C_6Me_6), 196.4 (s, Ru-*C*O).

Supporting Information (see footnote on the first page of this article): (**2**, CCDC-925056; **3** CCDC-925055) and ^{31}P NMR monitoring reaction of **1** and dppe in deuterated acetone at room temperature.

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