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BIS-OLEFIN-RHODIUM(I) COMPLEXES OF A TRIPOD LIGAND WITH AN *O,O,O*-DONOR SET

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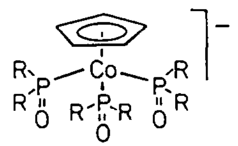
Summary

The organometallic anion $[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$ reacts as a tridentate oxygen ligand L^- with $[\{RhCl(diolefin)\}_2]$ (diolefin = 1,5-cyclooctadiene, norbornadiene, tetrafluorobenzobarrelene, trimethyltetrafluorobenzobarrelene, duroquinone) and with $[\{RhCl(C_2H_4)_2\}_2]$ in hexane or in acetone in the presence of $AgClO_4$ to give air stable compounds of the type [LRh(diolefin)] and $[LRh(C_2H_4)_2]$. These novel five-coordinate Rh^I complexes are fluxional molecules. They have been characterized by elemental analysis, and ^1H NMR, IR and mass spectroscopy.

Introduction

Stable Rh^I complexes of the type $[L'Rh(olefin)_2]$ (L′ = a six electron donor, such as cyclopentadienyl [1], pentamethylcyclopentadienyl [2], benzene, or substituted arene) [3–11] have been described. We recently demonstrated that the oxygen tripod ligands $L^- = [(C_5H_5)Co\{P(O)R_2\}_3]^-$ unlike most other oxygen ligands, form very stable metal carbonyl complexes [12,13].

$L^- \equiv$ 

The electronic properties of this six-electron ligand L^- must obviously be very

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different from those of $C_5H_5^-$, $C_5Me_5^-$ or arenes. We were therefore interested to see whether complexes of the type [(oxygen tripod ligand)Rh(olefin)$_2$] could be isolated, and, if so, what properties such complexes might have.

Results and discussion

The neutral Rh^I complexes [LRh(olefin)$_2$] ($L^- = [(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$; (olefin)$_2$ = 1,5-cyclooctadiene (COD) (I), norbornadiene (NBD) (II), tetrafluorobenzobarrelene (TFB) (III), trimethyltetrafluorobenzobarrelene (Me$_3$TFB) (IV), duroquinone (DQ) (V), and [LRh(C_2H_4)$_2$] (VI) were prepared according to eq. 1.

$$1/2\left[\{\mathrm{RhCl(olefin)_2}\}_2\right] + \mathrm{NaL} \xrightarrow{\text{hexane}} \left[\mathrm{LRh(olefin)_2}\right] + \mathrm{NaCl} \qquad (1)$$

The preparations of the compounds I–V were carried out in boiling hexane, but the ethylene complex VI had to be prepared at room temperature. The cyclooctadiene complex (I) was also synthetized in good yield in water at room temperature but the reaction took several days. A good alternative method for the synthesis of the compounds I and VI is shown in eq. 2.

$$1/2\left[\{\mathrm{RhCl(olefin)_2}\}_2\right] + \mathrm{AgClO_4} + \mathrm{NaL} \xrightarrow{\text{acetone, 25°C}}$$

$$\left[\mathrm{LRh(olefin)_2}\right] + \mathrm{NaClO_4} + \mathrm{AgCl} \qquad (2)$$

The oxygen tripod complexes I–VI were all obtained as yellow to orange crystalline air-stable solids. Their compositions were confirmed by their elemental analyses and mass spectra (see Experimental).

The IR spectra of I–VI are dominated by the typical pattern of the tripod ligand L^- [14]. The P=O stretching frequency is observed at 1100–1140 cm^{-1}, at lower wave numbers than the corresponding band of the sodium salt NaL (ν(P=O) 1170 cm^{-1}). This is probably a result of a lowering of the P=O bond order upon coordination of the tripod ligand to the rhodium diolefin fragment. A similar shift to longer wavelengths has been observed upon coordination of L^- to $Mn(CO)_3^+$ and $Re(CO)_3^+$ [13]. The ν(C=O) vibration at 1620 cm^{-1} in the IR spectra of the duroquinone complex V is intensive and very much broader than that of free duroquinone. Such broadening or splitting of the C=O stretching vibration is indicative of a non-planar duroquinone ligand [15]. The X-ray structure of V has not yet been determined, but the crystal structure of the duroquinone complex [($C_6H_5CH_3$)Rh(DQ)]PF_6, which is isoelectronic with V, is known. It shows a distinct boat like deformation of the quinone ligand, as expected [16].

The ^1H NMR spectra of the rhodium complexes [LRh(olefin)$_2$] I–VI in $CDCl_3$ show the characteristic proton resonances of the coordinated olefins (Table 1). The signals from the coordinated oxygen tripod ligand L^- show only minor chemical shift differences. Otherwise they are identical with the ^1H NMR spectrum of NaL. This means that the rhodium(olefin)$_2$ unit rotates rapidly relative to the tripod ligand in all the [LRh(olefin)$_2$] complexes. If these molecules were rigid the local symmetry could be not higher than C_s, and at least three pairs of anisochronous OC_2H_5 groups would result. This anisochrony should be readily detected, since it is clearly observed, for example, in the spectrum of [LMo(CO)$_2$NO], where the Mo(CO)$_2$NO unit is rigid relative to the tripod ligand L [12].

TABLE 1

100 MHz ^1H NMR DATA FOR THE COMPLEXES [LRh(olefin)$_2$] (I–VI)[a] IN $CDCl_3$ (δ in ppm, TMS int.)

Complex	Signals	Assignment
[LRh(COD)] (I)	1.60, 2.60(s)	8H, CH_2
	3.62(m)	4H, HC=CH
[LRh(NBD)] (II)	0.98(s)	2H, CH_2
	3.20(s)	4H, HC=CH
	3.65(s)	2H, CH
[LRh(TFB)] (III)	2.65(s)	4H, HC=CH
	5.36(m)	2H, CH
[LRh(Me$_3$TFB)] (IV)	1.18(s)	6H, CH_3
	2.09(s)	2H, HC=CH
	2.42(d)	3H, CH_3
	4.66(s)	1H, CH
[LRh(DQ)] (V)	1.46(s)	12H, CH_3
[LRh(C_2H_4)$_2$] (VI)	2.39(s)	8H, H_2C=CH_2

[a] Signals of L^- in I–VI: δ (ppm) 1.3 (t, ^3J(HCCH) 7 Hz, 18H, CH_3); 4.1 (m, 14 lines, 12H, OCH_2); 5.0 (s, 5H, C_5H_5).

The ^1H NMR spectrum of complex VI at room temperature shows one broad signal at δ 2.4 ppm due to the eight ethylene protons. This indicates another dynamic process, the rotation of the olefins about the rhodium–olefin bond axis at an intermediate rate on the NMR time scale. At −30°C the rotation is sufficiently slow to show two separate signals at δ 1.8 and δ 2.9 ppm of the "inner" and "outer" olefin protons. The coalescence temperature is about 0°C. Two observations are noteworthy. First the olefin rotation is independent of the much faster rotation of the Rh(olefin)$_2$ unit relative to the tripod ligand L; even at −30°C this latter rotation is fast on the NMR time scale. Second, the isochrony of the signals of the "inner" and "outer" olefin protons at room temperature is not influenced by free ethylene. Whereas the olefin rotation takes place at an intermediate rate at room temperature the intermolecular exchange of ethylene is very slow. The free energy of activation for the ethylene rotation in VI, calculated from the expression

$$\Delta G^{\ddagger}_{T} = -RT \ln \frac{\pi \Delta\nu \cdot h}{\sqrt{2}\, kT},$$

is about 54 kJ mol^{-1} (T is coalescence temperature (K), $\Delta\nu$ is the chemical shift difference of the "inner" and "outer" ethylene protons in absence of exchange (s^{-1}), h is Planck's constant, k is Boltzmann's constant and R is the gas constant). The NMR and thermodynamic data for VI and comparable Rh^I ethylene complexes are given in Table 2.

Comparison of the data for various complexes in Table 2 suggests that the rate of olefin rotation decreases with increasing electron donation of the ligands relative to the ethylene ligands. This should lead to more rhodium to olefin π-back-bonding, thereby increasing the barrier for olefin rotation. The oxygen tripod ligand is obviously a weaker electron donor than the cyclopentadienyl in Table 2. The relative

TABLE 2

NMR DATA AND ACTIVATION PARAMETERS FOR Rh^I ETHYLENE COMPLEXES

Complex	$\delta(H_i)$ (ppm)	$\delta(H_o)$ (ppm)	Coalescence temp. (°C)	$\Delta G^{\ddagger}_{T}$ (kJ mol^{-1})	Ref.
$[LRh(C_2H_4)_2]$ [a] (VI)	1.80	2.90	0	54	–
$[(C_5H_4CN)Rh(C_2H_4)_2]$ [a]	1.45	3.12	22	59	17
$[(C_5H_5)Rh(C_2H_4)_2]$ [a]	1.03	2.86	55	66	17
$[(C_5Me_5)Rh(C_2H_4)_2]$ [b]	1.37	1.87	> 60	> 71	17

Solvents: [a] $CDCl_3$. [b] $C_6H_5OC_6H_5$.

donor strength cannot, however, be judged independently of the metal. We have found that the oxygen tripod ligand L^- in $[LMo(CO)_3]^-$ is a much stronger donor than the cyclopentadienyl ligand in $[CpMo(CO)_3]^-$ [12]. As more organometallic derivatives of the oxygen tripod ligand L^- become available a more quantitative comparison of the donor properties of L^- and Cp^- as a function of the *d*-electron energies will be possible.

The complexes I, II, III, and VI react with carbon monoxide at one atmosphere pressure in dichloromethane at ambient temperature, and complete replacement of the olefin ligands takes place within a few minutes. The reactions can be monitored by IR spectrosopy. The appearance of two $\nu(CO)$ vibrations at 2080 and 1990 cm^{-1} is consistent with the formation of a *cis*-dicarbonyl complex of the type $[LRh(CO)_2]$. When the solvent is rapidly evaporated the corresponding starting compounds, i.e. the diolefin complexes I, II, and III, are regenerated. The carbon monoxide–olefin exchange is obviously a rapid reversible process, and the equilibrium can be shifted to the right (eq. 3) when the mixture is kept under CO. $[LRh(CO)_2]$ can also be synthesized directly from $[\{RhCl(CO)_2\}_2]$ and NaL. It is not stable at room temperature in solution but slowly undergoes partial decarbonylation to yield the dinuclear complex $[LRh(\mu\text{-}CO)_3RhL]$ (eq. 4).

$$[LRh(diolefin)] + 2\,CO \xrightleftharpoons{CH_2Cl_2} [LRh(CO)_2] + diolefin \qquad (3)$$

$$2[LRh(CO)_2] \rightarrow [LRh(\mu\text{-}CO)_3RhL] + CO \qquad (4)$$

The structure of this dimer, formally containing an Rh–Rh single bond, has recently been determined by X-ray diffraction [18].

We are now studying oxidative addition reactions of $[LRh(olefin)_2]$ and $[LRh(CO)_2]$ and the reactions of these Rh^I complexes with electrophiles, to see how the tridentate oxygen ligand L^- influences the chemistry in comparison with the isoelectronic $C_5H_5^-$ and $C_5Me_5^-$ ligands.

Experimental

All reactions were carried out in Schlenk tubes under purified nitrogen. Reagent grade solvents were dried and distilled before use. $RhCl_3 \cdot aq$ and $[\{RhCl(C_2H_4)_2\}_2]$ were obtained from Strem Chemical Inc.; TFB [19], Me_3TFB [20], $[\{RhCl(diolefin)\}_2]$ (diolefin = COD [21], NBD [22], TFB, Me_3TFB [23], DQ [24], and NaL [25] were prepared by published procedures. IR and ^1H NMR spectra were recorded using

Perkin–Elmer PE 567, PE 580, Varian XL-100 and Bruker WP 80 spectrometers. Mass spectra were measured on a Varian MAT CH-5 spectrometer.

[LRh(diolefin)], $L^- = [(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$, diolefin = COD (I), NBD (II), TFB (III), Me_3TFB (IV), DQ (V)

Method 1. A slurry of 0.1 mmol of the relevant dimeric complex [{RhCl(diolefin)}$_2$] and 0.22 mmol NaL in 25 ml hexane was heated under reflux for 24 h. The solvent was removed under reduced pressure and the solid residue washed with water and dried in vacuo. The products can be recrystallized from acetone/pentane. Yield ~ 75%.

Method 2. 0.4 mmol NaL and 0.4 mmol $AgClO_4$ were added to a solution or suspension of 0.2 mmol ({RhCl(diolefin)}$_2$] in 25 ml acetone. The mixture was stirred for 1 h in the dark, then the AgCl was filtered off using kieselgur, and the filtrate was evaporated to dryness. The solid residue was purified as above. Yield 50–60%.

[LRh(COD)] (I): Found: C, 37.84; H, 5.98. $C_{25}H_{47}CoO_9P_3Rh$ calcd.: C, 37.87; H, 5.93%. Mp. 116°C. IR(KBr, ν(P=O)): 1145 cm^{-1}.

[LRh(NBD)] (II): Found: C, 38.02; H, 5.76. $C_{24}H_{43}CoO_9P_3Rh$ calcd.: C, 39.47; H, 5.93%. Mp. 104°C. IR(KBr, ν(P=O)): 1104 cm^{-1}.

[LRh(TFB)] (III): Found: C, 40.07; H, 4.65. $C_{29}H_{41}CoF_4O_9P_3Rh$ calcd.: C, 40.30; H, 4.78%. Mp. 184°C. IR(KBr, ν(P=O)): 1144 cm^{-1}. MS: *m/e* 864 (M^+, 100%), 638 (M^+ – TFB, 42%).

[LRh(Me_3TFB)] (IV): Found: C, 42.21; H, 5.07. $C_{32}H_{47}CoF_4O_9P_3Rh$ calcd.: C, 42.40; H, 5.23%. Mp. 134°C. IR(KBr, ν(P=O)): 1145 cm^{-1}. MS: *m/e* 906 (M^+, 100%), 638 (M^+ – Me_3TFB, 43%).

[LRh(DQ)] (V): Found: C, 40.51; H, 5.93; P, 11.37. $C_{27}H_{47}CoO_{11}P_3Rh$ calcd.: C, 40.41; H, 5.90; P, 11.58%. Mp. 252°C (d). IR(KBr): ν(P=O) 1130; ν(C=O) 1620 cm^{-1}.

[LRh$(C_2H_4)_2$] (VI), $L^- = [(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$

Method 1. A slurry of 65.8 mg (0.2 mmol) of the dimeric complex [{RhCl$(C_2H_4)_2$}$_2$] and 245.3 mg (0.44 mmol) NaL in 25 ml hexane was stirred at room temperature for 24 h. After filtration the solvent was removed under reduced pressure and the solid residue was washed with water and dried in vacuo. Recrystallization from pentane, yield 58%.

Method 2. A solution of 83 mg (0.4 mmol) $AgClO_4$ in 5 ml acetone was added to a slurry of 65.8 mg (0.2 mmol) [{RhCl$(C_2H_4)_2$}$_2$] and 223 mg (0.4 mmol) NaL in 25 ml acetone at –10°C. After one hour stirring in the dark, AgCl was filtered off using kieselgur. The filtrate was evaporated to dryness and the solid residue purified as above. Yield 45%. Found: C, 35.72; H, 5.66. $C_{21}H_{43}CoP_3O_9Rh$ calcd.: C, 36.33; H, 6.24%. IR(KBr, ν(P=O)): 1103 cm^{-1}. MS: *m/e* 694 (M^+, 24%), 666 (M^+ – C_2H_4, 46%), 638 (M^+ – $2C_2H_4$, 100%).

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