Journal of Organometallic Chemistry, 221 (1981) 351—360
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE REACTIVITY OF COMPLEXED CARBOCYCLES

XIII *. CATIONIC DIMETALLIC COMPLEXES WITH BRIDGING CYCLOOCTATETRAENE: SYNTHESIS AND FLUXIONAL BEHAVIOUR

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(Received June 15th, 1981)

Summary

The electron-rich cyclooctatetraene complexes $C_8H_8Fe(CO)_3$ (I), $C_5H_5CoC_8H_8$ (II) and $C_5H_5RhC_8H_8$ (III) have been treated with various unsaturated cationic organometallic compounds of rhodium, iridium and palladium to form dimetallic products in high yields. A common structural feature of the rhodium and iridium complexes is a metal—metal bond with bridging fluxional cyclooctatetraene and fluxional olefinic ligands. The palladium complexes have a static pseudo-triple-decker structure with tub-shaped cyclooctatetraene coordinating with two double bonds each to two different organometallic moieties. All the complexes were characterized by ^{13}C NMR spectroscopy. In the case of the fluxional molecules at low temperature the rotational movement of the terminal olefinic ligands is sufficiently slow for observation of the spectra at the slow exchange limit.

Introduction

We have previously demonstrated that the electron-rich cyclooctatetraene complexes $CpCoC_8H_8$ [Cp = cyclopentadienyl] and $C_8H_8Fe(CO)_3$ with two uncoordinated double bonds can be used as starting materials for the synthesis of heterodimetallic compounds [1]. These (18 + 4) *e* precursors, when treated with unsaturated 12*e* organometallic groups, yielded dimeric 34*e* complexes in which

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* For part XII see ref. 1. This article is also part XXX of the series ^{13}C NMR spectroscopy, for part XXIX see ref. 10.

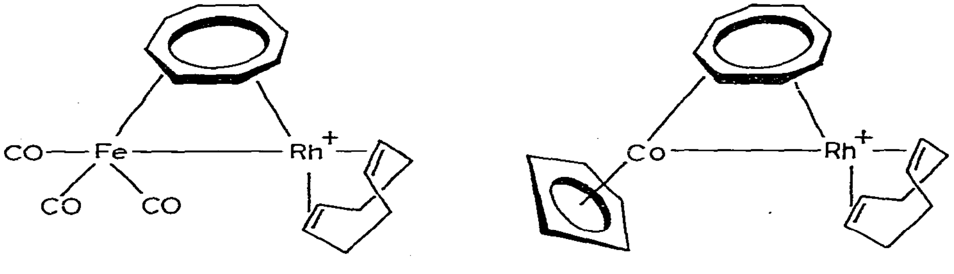
0022-328X/81/0000—0000/$02.50

both metals achieve a noble gas configuration through a metal—metal bond and a bridging cyclooctatetraene ligand. In extension of this work we set out to prepare cationic analogues of these compounds by a similar route namely reaction of the above (18 + 4)*e* complexes with cationic organometallic groups such as $[C_8H_{12}Rh]^+$, $[C_7H_8Rh]^+$ and others described by Schrock and Osborn [2].

These coordinatively unsaturated species are easily generated in weakly coordinating solvents by treatment of the dimeric halide complexes with silver salts. They can be regarded as 12*e* moieties, although they are probably stabilized by weak interaction with solvent molecules. Solutions of these species, when treated with various donor ligands (e.g., phosphines, arenes and diolefins) have been reported to yield four- or five-coordinated complexes in high yield [2]. We assumed that this reaction could be extended to the above mentioned π-electron donating species, which are capable of acting as six-electron donors. The complexes formed in this way should either have a metal—metal bond and bridging fluxional cyclooctatetraene or, possibly, a triple-decker structure with cyclooctatetraene sandwiched between two metals.

Results and discussion

Treatment of pale yellow solutions of $[CODRh]BF_4$ (A) [COD = cyclooctadiene] in acetone with $C_8H_8Fe(CO)_3$ (I) or $CpCoC_8H_8$ (II) immediately gave red-brown crystalline precipitates. They were insoluble in ether, but readily dissolved in polar solvents such as nitromethane. Elemental analyses confirmed the expected composition $[(CO)_3FeC_8H_8RhC_8H_{12}]BF_4$ (IA) and $[C_5H_5CoC_8H_8RhC_8H_{12}]BF_4$ (IIA). In the noise-decoupled ^{13}C NMR spectrum at room temperature complex IA exhibits a sharp doublet at 75.7 ppm (J(Rh, C) = 2 Hz) for the cyclooctatetraene ring and several broad signals apparently due to coordinated cyclooctadiene. Complex IIA shows similar spectroscopic features in having sharp signals for the cyclopentadienyl and cyclooctatetraene ring, but almost undetectable broad lines for the COD ligand. This suggests that a fluxional movement of cyclooctadiene occurs in these molecules, the recorded spectra being close to the coalescence point. On cooling the signal began to sharpen, and the limiting spectrum was reached at about −60°C. It now shows for both compounds two sharp doublets for the olefinic carbons of COD and two singlets in the aliphatic region, indicating that cyclooctadiene occupies two nonequivalent coordination sites. The low-temperature spectrum



IA IIA

Fig. 1. Structural formulae for IA and IIA.

is clearly irreconcilable with a symmetrical triple-decker structure, but compatible with a molecular framework containing a heterodimetallic bond with bridging fluxional cyclooctatetraene, as shown in Fig. 1. These complexes are, therefore, similar in structure to the previously described dimetallic compounds, e.g., $CpCoC_8H_8Mo(CO)_3$ [1]. The rhodium complex $CpRhC_8H_8$ (III), although unreactive towards reagents like (diglyme)$Mo(CO)_3$, also immediately formed a dimeric species $[CpRhC_8H_8RhC_8H_{12}]BF_4$ (IIIA) upon treatment with $[CODRh]BF_4$. Based on the structure of the molecule, one would expect that the resonance signal of the bridging cyclooctatetraene would show couplings to two nonequivalent rhodium nuclei. This was found to be the case in the ^{13}C NMR spectrum of IIIA (Fig. 2), in which the carbon resonance of cyclooctatetraene is split into four equidistant lines (Fig. 3).

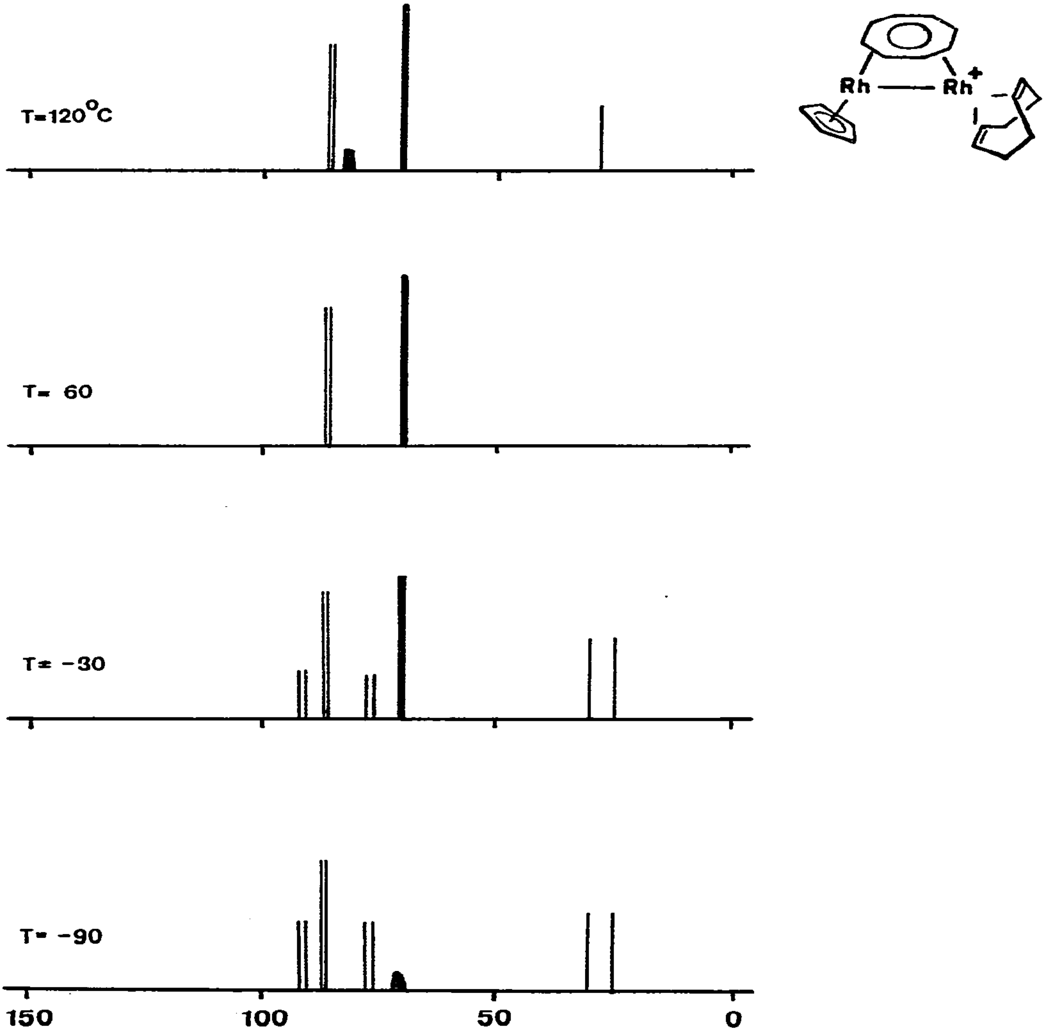


Fig. 2. Temperature-dependent schematic ^{13}C NMR spectra of IIIA (50.3 MHz, CH_2Cl_2).

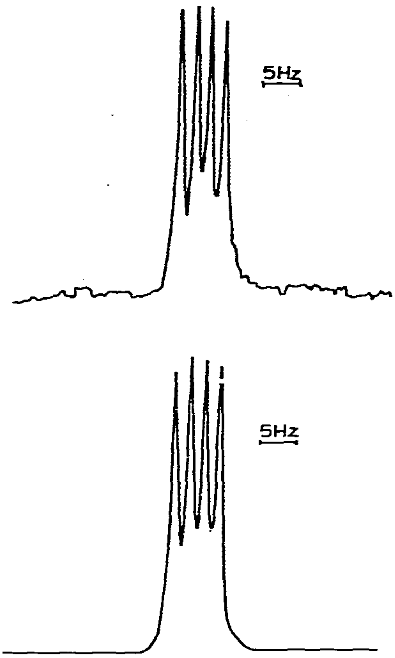
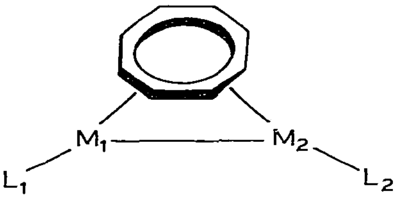


Fig. 3. Observed ^{13}C NMR signal of cyclooctatetraene in IIIA (recorded with high digital resolution) (top), and simulated signal (below). Arbitrary parameters (in Hz) for the simulation were: $\nu_A = 20$; $\nu_M = 3000$; $\nu_X = 30\,000$; $J_{AX} = 4$; $J_{MX} = 2$.

Since we could independently obtain the chemical shifts for the two different ^{103}Rh nuclei by direct observation at 2.83 MHz [3], we were able to simulate this multiplet (X part of AMX-system). Figure 2 also shows the temperature dependent ^{13}C spectra. Because of the large shift difference for the two olefinic signals of the cyclooctadiene part we were unable to reach the fast exchange limit for the fluxional molecules I—IIIA, as decomposition sets in above 100°C.

In extension of this work we also explored the reactivity of other unsaturated organometallic groups. In situ generation of [NBDRh]BF$_4$ (B) [NBD = norbornadiene] in acetone and subsequent treatment with I, II or III produced dark-brown to red crystalline solids IB, IIB and IIIB in very good yields. Apart from the sharp lines for the cyclopentadienyl and cyclooctatetraene carbons, the ^{13}C NMR spectra for these compounds at room temperature also show sharp signals for the norbornadiene ligand, including a single resonance for the four olefinic carbons. As it seems unlikely that these complexes have a molecular structure different from the cyclooctadiene compounds, we assume that full fluxionality on the NMR time scale occurs even at room temperature. This was confirmed by low temperature measurements, where, for complex IIIB, for instance, the signal of the olefinic carbons of norbornadiene began to broaden and disappeared at —40° C, with two new signals reemerging at —65° C. The limiting spectrum was reached at —80°C, now showing norbornadiene to occupy two non-equivalent sites. At —120° C, the lowest temperature we could reach for these complexes for solubility reasons, the signal of the bridging cyclooctatetraene started to collapse. A third unsaturated group that we used to build up dimetallic compounds was the dicarbonylcation $[(CO)_2Rh]BF_4$ (C). This produced the dimeric compounds $[(CO)_3FeC_8H_8Rh(CO)_2]BF_4$ (IC), $[CpCoC_8H_8Rh(CO)_2]BF_4$ (IIC) and $[CpRhC_8H_8Rh(CO)_2]BF_4$ (IIIC) in equally good yields as light-red crystalline precipitates. An analogous complex to IC, the isoelectronic neutral tropylium compound $(CO)_3FeC_7H_7Rh(CO)_2$, was previously described by Takats [4]. The X-ray structure of that complex revealed that the two carbonyl groups bound to rhodium occupy equivalent coordination sites *trans* to the bridging tropylium ring. We observe one doublet in the ^{13}C NMR for the dicarbonylrhodium group (J(Rh, C) ~80 Hz) in all three complexes and one singlet for the tricarbonyliron group in IC which remained unchanged on cooling to −55°C.

As a final example for this class of dimetallic compounds we managed to prepare an iridium complex $[CpCoC_8H_8IrC_8H_{12}]BF_4$ (IID) by treatment of



M_2 = Rh, M_1 = Fe, L_1 = $(CO)_3$, L_2 = COD (IA)
L_2 = NBD (IB)
L_2 = $(CO)_2$ (IC)
M_2 = Rh, M_1 = Co, L_1 = Cp L_2 = COD (IIA)
L_2 = NBD (IIB)
L_2 = $(CO)_2$ (IIC)
M_2 = Rh, M_1 = Rh, L_1 = Cp L_2 = COD (IIIA)
L_2 = NBD (IIIB)
L_2 = $(CO)_2$ (IIIC)
M_2 = Ir, M_1 = Co, L_1 = Cp L_2 = COD (IID)

$[CODIr]BF_4$ (D) with $CpCoC_8H_8$. Its spectroscopic features are completely analogous to those of the rhodium complex IIA, the limiting spectrum for the cyclooctadiene rotation being reached at −50°C.

The ^{13}C NMR shift data for all complexes described here are listed in Table 1. With the limited digital resolution in our spectra, Rh, C coupling constants can only be reported with an accuracy of ±1 Hz, and the following typical values have been observed: Cp: (6); olefinic carbons: (8—10); aliphatic carbons in norbornadiene: (6) for bridgehead carbons, (2) for methylene groups; CO: (80); cyclooctatetraene: (2) in IA—IC and IIA—IIC. The two nonequivalent Rh atoms in IIIA—IIIC are coupled to the cyclooctatetraene carbons with 4 Hz and 2 Hz, respectively.

In the temperature-dependent ^{13}C NMR spectra coalescence points were observed for the exchanging carbon atoms of the olefinic ligands (COD, NBD), and estimated $\Delta G_c^{\neq}$ values are about 20 kJ/mol higher for the rhodium-bound cyclooctadiene than for the rhodium-bound norbornadiene.

TABLE 1

^{13}C NMR DATA FOR COMPLEXES IA—IC, IIA—IID, IIIA—IIIC; PROTON-NOISE-DECOUPLED. (Chemical shift in ppm relative to TMS, 50.3 MHz.)

Complex	T(°C)	Assignment					
		COT	Cp	CO	Olefinic	Aliphatic	
IA	70 ^{a}	75.7(d)			92.1 ^{g}	32.3(s)	
	−60 ^{b}	75.2 ^{g}		211.0(s)	94.1(d)	32.8(s)	
					86.3(d)	30.4(s)	
IB	30 ^{b}	76.3(d)		211.2(s)	56.8(d)	60.1(d)	47.5(d)
	−95 ^{c}	75.7 ^{g}		210.9(s)	56.7(d)	59.6(d)	46.7(s) ^{f}
					53.9(d)		
IC	−55 ^{b}	74.9(d)		210.3(s)			
				184.5(d)			
IIA	70 ^{a}	70.0(d)	83.6(s)		84 ^{g}	32 ^{g}	
	−60 ^{b}	70 ^{g}	82.8(s)		89.6(d)	33.0(s)	
					78.8(d)	30.2(s)	
IIB	30 ^{b}	69.4(d)	83.5(s)		53.6(d)	60.1(d)	49.1(d)
	−80 ^{d}	67.8 ^{g}	81.9(s)		54.0(d)	59.5(d)	48.4(s) ^{f}
					50.9(d)		
IIC	30 ^{b}	69.5(d)	83.1(s)	186.4(d)			
IID	−50 ^{b}	66 ^{g}	83.7(s)		85.5(s)	34.6(s)	
					73.8(s)	31.5(s)	
IIIA	120 ^{e}	68.7(m)	84.5(d)		82 ^{g}	29.7(s)	
	−30 ^{d}	71.8(m)	87.8(d)		89.3(d)	34.5(s)	
					79.0(d)	32.3(s)	
IIIB	30 ^{b}	70.0(m)	83.5(d)		53.6(d)	60.1(d)	49.1(d)
	−95 ^{c}	69.1 ^{g}	81.9(d)		53.9(d)	59.5(s) ^{f}	48.4(s) ^{f}
IIIC	−30 ^{b}	70.2(m)	86.7(d)	187.0(d)	50.9(d)		

[a] In CD_3NO_2; [b] In acetone-d_6; [c] In Freon 21; [d] In CD_2Cl_2; [e] In DMSO-d_6. [f] Couplings not resolved due to the digital resolution. [g] Broad lines due to the dynamic process. (s) singlet; (d) doublet; (m) multiplet (X part of AMX-system, see Fig. 3).

The line drawings used in Figs. 1 and 2 to represent the overall molecular structure of the respective cobalt, iron and rhodium complexes do not, however, give a satisfactory description of the actual bonding mode in these compounds. Electron counting reveals that the CpCo, CpRh and $Fe(CO)_3$ units always have two electrons more in their valence shell than their cationic rhodium and iridium counterparts. If symmetrically bound to the bridging cyclooctatetraene, one metal group would, therefore, have two electrons less than the other. Only by electron exchange either through the metal—metal bond or through the bridging ligand can a balanced structure be achieved. Two possible bonding schemes emerge from these considerations:

(a) A donor metal—metal bond as observed in $CpCoC_8H_8Mo(CO)_3$;

(b) An unsymmetrical bonding mode of the bridging C_8H_8 ring.

The donor bond was clearly indicated in some of the previously described complexes by its spectroscopic and structural effects in the carbonyl group located *trans* to it [1].

We do not see evidence of a similar effect, indicative of a strong *trans*

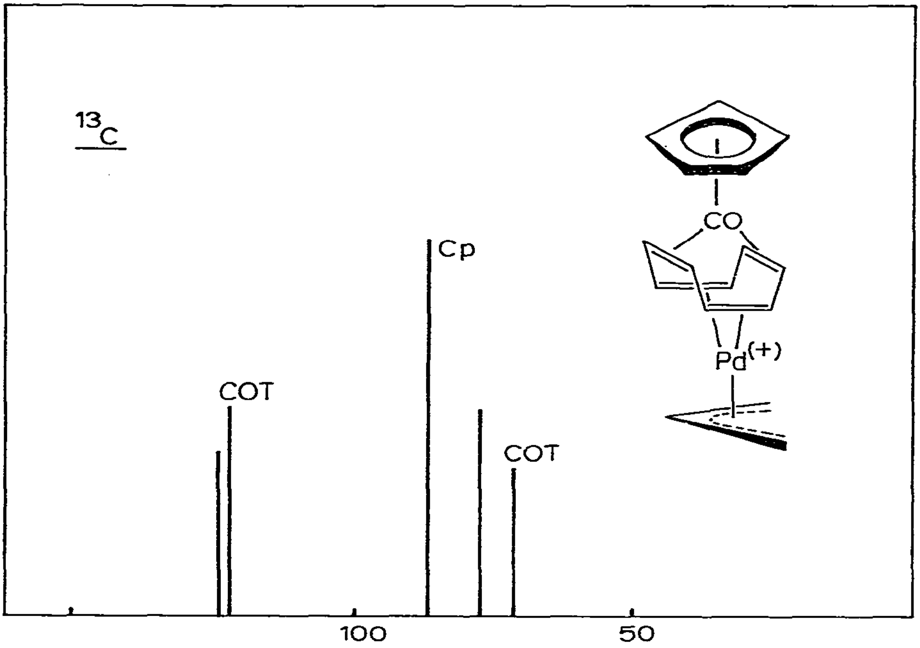


Fig. 4. ^{13}C NMR spectrum of IIE (25.2 MHz, cf. Table 2).

influence, in the IR spectra of the cationic carbonyl complexes IC—IIIC. In the olefin complexes IA—IIIA and IB—IIIB there is, however, significant difference in chemical shifts for the two nonequivalent double bonds of cyclooctadiene and norbornadiene. This might indicate that in these complexes one double bond is *trans* to the metal—metal bond and the other *trans* to cyclooctatetraene.

As we were not able to observe the lower limiting spectrum for the fluxional cyclooctatetraene moiety, the activation barrier for rearrangement being small as in other reported cases [5], we cannot exclude an unsymmetrical bonding mode of cyclooctatetraene for any of the described complexes. By coordination of five carbons to the 12*e* moiety and three to the 14*e* group, a balanced structure could also be achieved for all molecules. This arrangement would be similar to the unsymmetrical bonding mode observed in the complex $(CO)_3FeC_7H_7Rh(CO)_2$ [4], where, according to the X-ray structure, iron is bound to three carbons of the bridging tropylium ring, while the $Rh(CO)_2$ moiety, having one electron less, coordinates to four carbons. We are currently trying to grow single crystals of some complexes to clarify this point by X-ray structure analysis *.

Cationic rhodium(I) olefin complexes are generally susceptible to nucleophilic attack and displacement reactions by strong Lewis bases such as tertiary phosphines [6]. Our cationic dimeric complexes also underwent rapid reactions with alkylphosphines, but the displacement of ligands was not selective and led to mixtures of products. NMR spectra showed that along with dimetallic complexes such as $[CpCoC_8H_8Rh(PR_3)_2]^+$, monomeric compounds

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* *Note added in proof.* The X-ray structure of Ib does indeed show that the Rh(NBD) group coordinates to five carbons while the $Fe(CO)_3$ group is bound to three carbons of the COT unit.

TABLE 2

^{13}C NMR SPECTRA OF IIE AND IIF, PROTON NOISE-DECOUPLED, IN CD_3NO_2. (Chemical shifts in ppm relative to TMS, 25.2 MHz)

Complex	Assignment					
	Cp	C_8H_8/Co	C_8H_8/Pd	Allyl		
				C(1, 3)	C(2)	CH_3
IIE	87.4	71.7	122.8	77.1	124.9	—
IIF	87.5	71.7	122.5	76.3	141.4	22.9

$[Rh(PR_3)_4]^+$ were also formed. We were unable to suppress this side reaction or to separate the product mixtures. With less nucleophilic reagents like acetonitrile no substitution reactions were observed.

Further coordinatively unsaturated species we considered as suitable starting materials for the synthesis of dimetallic complexes were the palladium complexes [allylPd]BF_4 (E) and [2-methallylPd]BF_4 (F) [2]. They were again easily generated in acetone solution by halide abstraction from the dimeric $[allylPdCl]_2$ or $[2\text{-methallylPdCl}]_2$. After treating these solutions with $C_8H_8Fe(CO)_3$ no stable products could be isolated, but the addition of $CpCoC_8H_8$ resulted in the immediate precipitation of light-brown crystalline $[C_5H_5CoC_8H_8PdC_3H_5]BF_4$ (IIE) and $[C_5H_5CoC_8H_8PdC_4H_7]BF_4$ (IIF) in almost quantitative yields. To our surprise these complexes were not structurally similar to the other dimetallic species. According to the ^{13}C NMR spectra they have a "pseudo-triple-decker" structure, in which cyclooctatetraene maintains a tub conformation, allowing the two independent metal atoms cobalt and palladium their favoured chelating coordination. Because of the different chemical environments we see a large shift difference for cyclooctatetraene carbons attached to cobalt in comparison to those bound to palladium (Fig. 4, Table 2). Palladium, thus appears to remain coordinatively unsaturated in these dimetallic complexes, and not to achieve a noble gas configuration. Structurally, IIE and IIF are similar to the previously described complex $CpCoC_8H_8Mo(CO)_4$ [1]. Treatment with various Lewis bases quantitatively displaced the $CpCoC_8H_8$ unit with formation of the well known complexes $[allylPdL_2]^+$ [2].

Conclusion

The present study was undertaken to investigate the utility of cyclooctatetraene complexes with uncoordinated double bonds as starting materials for the synthesis of heterodimetallic compounds. It was demonstrated that a wide variety of complexes are accessible by this route in very good yields. They represent the first examples of such complexes with bridging cyclooctatetraene. Because of the unequal number of electrons in the two metal centers, some form of electron exchange may occur. This is probably achieved either by the donation of electrons from the "electron-rich" metal into a donor metal—metal bond or by an unsymmetrical bonding mode of the mutual cyclooctatetraene ligand.

A series of similar dimetallic complexes with a bridging tropylium ligand will be discussed in a later paper [7].

Experimental

All experiments were carried out under nitrogen, using solvents purified under nitrogen by standard procedures. NMR measurements were performed on Varian XL-100 and XL-200 spectrometers. IR spectra were recorded on a Beckman IR 12 apparatus.

$(CO)_3FeC_8H_8$ [8], $C_5H_5CoC_8H_8$ [8] and $C_5H_5RhC_8H_8$ [9] were prepared by literature procedures.

(a) IA, IB, IC

0.50 g (2.0 mmol) $(CO)_3FeC_8H_8$ in 15 ml acetone is treated with 0.60 g (2.0 mmol) $[L_2Rh]BF_4$ in 15 ml acetone (the latter complex is prepared by reaction of 2.0 mmol $[L_2RhCl]_2$ with 4.0 mmol $AgBF_4$ in THF or acetone.) The colour of the solution changes immediately from yellow to red. After 2 hours stirring the formed precipitates are filtered off and washed with hexane. They can be recrystallized from acetone. All three compounds decompose above 100°C. Yield of IA: 0.70 g (64%), yield of IB: 0.82 g (75%), yield of IC: 0.88 g (80%).

(IA) Found: C, 42.04; H, 3.72; Rh, 19.17; Fe, 9.96; F, 13.96. $C_{19}H_{20}BF_4FeO_3Rh$ calcd.: C, 42.10; H, 3.69; Rh, 19.00; Fe, 10.03; F, 14.03%.

(IB) Found: C, 42.10; H, 3.93. $C_{18}H_{16}BF_4FeO_3Rh$ calcd.: C, 42.20; H, 3.87%.

(IC) Found: C, 31.77; H, 1.63; Fe, 11.36; F, 15.36. $C_{13}H_8BF_4FeO_5Rh$ calcd.: C, 31.87; H, 1.64; Fe, 11.40; F, 15.32% IR (CH_2Cl_2): 2108, 2072, 2057, 2023, 1987 cm^{-1}.

(b) IIA, IIB, IIC

The procedure is as under (a), but with 0.46 g (2.0 mmol) $C_5H_5CoC_8H_8$ instead of $(CO)_3FeC_8H_8$. The dark red precipitates can be recrystallized from a mixture of nitromethane and diethyl ether. The compounds decompose above 100°C. Yield IIA: 0.69 g (61%), yield of IIB: 0.54 g (49%), yield of IIC: 0.63 g (54%).

(IIA) Found: C, 47.50; H, 4.67; Co, 11.11; Rh, 19.26; F, 14.25. $C_{21}H_{25}BCoF_4Rh$ calcd.: C, 47.90; H, 4.75; Co, 11.19; Rh, 19.42; F, 14.49%.

(IIB) Found: C, 47.85; H, 4.98. $C_{20}H_{21}BCoF_4Rh$ calcd.: C, 47.60; H, 4.86%.

(IIC) $C_{15}H_{13}BCoF_4O_2Rh$. IR (CH_2Cl_2): 2075, 2030 cm^{-1}.

(c) IID, IIE, IIF

The procedure for IID is the same as for IIA, but with 2.0 mmol $[C_8H_{12}Ir]BF_4$. The yield of IID is 0.92 g (75%).

The synthesis of IIE and IIF is by the same route, using $[allylPd]BF_4$ and $[2\text{-methylallylPd}]BF_4$. After 1 hour of stirring the precipitates are filtered off and washed with hexane. Yield of IIE: 0.66 g (72%), yield of IIF: 0.65 g (68%). (IID) and (IIE) were characterized by ^{13}C NMR (Table 2). (IIF) Found: C, 41.53; H, 4.00; F, 15.32; Co, 12.04. $C_{17}H_{20}BCoF_4Pd$ calcd.: C, 42.85; H, 4.23; F, 15.95; Co, 12.37%.

(d) IIIA, IIIB, IIIC

0.30 g (1.0 mmol) $C_5H_5RhC_8H_8$ in 15 ml acetone is treated with 0.30 g (1.0 mmol) $[L_2Rh]BF_4$ in 15 ml acetone and the mixture stirred for 4 hours, during which the colour changes from orange to deep red. The solvent is evaporated and the residue washed with hexane then taken up in CH_2Cl_2. After addition of diethyl ether the complexes crystallize out at —30°C. They decompose above 100°C. Yield of IIIA: 0.40 g (66%), yield of IIIB: 0.39 g (64%), yield of IIIC: 0.48 g (79%).

(IIIA) Found: C, 44.47; H, 3.86. $C_{21}H_{25}BF_4Rh_2$ calcd.: C, 44.52, H, 3.71%.
(IIIB) Found: C, 44.51; H, 4.05. $C_{20}H_{21}BF_4Rh_2$ calcd.: C, 44.63; H, 4.01%.
(IIIC) $C_{15}H_{13}BF_4O_2Rh_2$ IR (CH_2Cl_2): 2070, 2026 cm^{-1}.

Acknowledgements

This work was supported by the Swiss National Science Foundation. A generous gift of cyclooctatetraene by BASF Ludwigshafen is gratefully acknowledged.

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