force constants and be indicated by negative σ values. It is at once evident from Figure 3 that there is little correlation between the basicities of the free ligands and their position on the σ scale. We suggest that what the σ parameter measures is the donor property of the ligand *as it exists in the complex, modified by synergic effects.* Thus the π-acceptor portion of the Mo–CO bond would enhance donation of the normally nonbasic lone pair on the carbon atom, while the π-donor component of the Mo–$OCHNR_2$ bond would diminish the tendency of this ligand to donate its lone pair. Figure 3 shows that, in general, as in the manganese derivatives, strong π-donor ligands tend to be poor σ donors, and conversely.

It seems unlikely that the σ component of bonds involving these neutral, lone-pair donating ligands could undergo any reversal of sense as postulated for the manganese derivatives.[33] For ligands at the lower right of Figure 3, this implies that both σ and π components are tending to move electron density toward molybdenum. This is consistent with the generally low stability of such complexes and their low solubility in nonpolar solvents.

Conclusions.—In a simplified approach to a very complicated bonding situation, we have been able to proceed from a few reasonable assumptions to develop crude scales of σ and π donor–acceptor ability. The general principle, which is that carbonyl groups *cis* and *trans* to L will respond differently to changes in the σ- and π-bonding properties of the ligand, should be capable of further refinement. One obvious need is for improved carbonyl stretching force constants, and it appears that this need is being met.[21]

In general, we might expect a relation between the Δk's to have the form $\Delta k_2 = \Delta\sigma + \Delta\pi$ and $\Delta k_1 = m\Delta\sigma + n\Delta\pi$. We have taken $m = 1$ and $n = 2$, but more sophisticated considerations may suggest other values, which would of course alter the scales. Small changes in m and n, however, should not seriously alter the general ordering of ligands proposed here.

Acknowledgment.—We are indebted to our coworkers for synthesis and infrared spectra of many of the compounds in Table II which prompted this paper. We thank especially Mr. R. S. Gay for helpful discussions and for executing the force constant calculations. We are greatly indebted to Professor T. L. Brown for making available his infrared data in advance of publication and for discussions. The work was supported by the National Research Council of Canada.

[33] This can be seen by considering resonance structures for the σ bond. In $LMn(CO)_5$, the canonical forms are

$$\underset{\text{III}}{L^-{:}Mn(CO)_5{}^+} \longleftrightarrow \underset{\text{IV}}{L{-}Mn(CO)_5} \longleftrightarrow \underset{\text{V}}{L^+{:}Mn(CO)_5{}^-}$$

Form III will make a larger contribution at the expense of V as the electronegativity of L increases, ultimately reversing sense. For $LMo(CO)_5$, the only reasonable forms to describe the σ bond are $L{:}Mo(CO)_5 \longleftrightarrow L^+{-}Mo(CO)_5{}^-$. A form $L^-{::}Mo^+$ (corresponding to sense reversal) would involve σ^* orbitals or σ orbitals from a higher quantum level, neither one an attractive possibility.

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Cyclooctatetraene–Rhodium(I) Complexes

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The known, dimeric complex of cyclooctatetraene (C_8H_8) with rhodium(I), $[C_8H_8RhCl]_2$, is conveniently prepared by displacing cyclooctene from its rhodium(I) complex, $(C_8H_{14})_2RhCl$, with cyclooctatetraene. The chlorine bridges of $[C_8H_8RhCl]_2$ are split by pyridine and triphenylphosphine giving monomeric complexes of formula C_8H_8RhCl(ligand) and by 2,4-pentanedione (acetylacetone, acacH) in the presence of base giving monomeric C_8H_8Rh(acac). Infrared and proton nmr spectroscopic data suggest that in these compounds the eight-membered ring has a tub conformation and is coordinated to the metal *via* the 1,5 double bonds, the 3,7 double bonds being free. In solution, the complex $[C_8H_8RhCl]_2$ decomposes to give a brown, insoluble, probably polymeric compound of formula $[C_8H_8Rh_2Cl_2]_n$. This reacts with pyridine and triphenylphosphine giving complexes of formula $C_8H_8Rh_2Cl_2(\text{ligand})_2$ and with 2,4-pentanedione in the presence of base giving $C_8H_8Rh_2(\text{acac})_2$. In these compounds, tub-shaped cyclooctatetraene probably bridges a pair of rhodium atoms *via* its 1,5 and 3,7 double bonds.

Introduction

Metal–cyclooctatetraene complexes are of particular interest owing to the variety of ways in which metal–ring bonding can take place.[2] Only three such complexes of rhodium(I) have so far been reported: $[C_8H_8RhCl]_2$,[3,4] $C_8H_8RhC_5H_5$,[5] and $C_8H_8Rh_2(C_5H_5)_2$.[6] Subsequent attempts to repeat the preparation of $[C_8H_8RhCl]_2$ from rhodium(III) chloride and cyclooctatetraene[3,4] have not been successful, and a reinvestigation

[1] Research School of Chemistry, Australian National University, Canberra, Australia.

[2] M. A. Bennett, *Advan. Organometal. Chem.*, **4**, 353 (1966).

[3] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

[4] M. A. Bennett and G. Wilkinson, *ibid.*, 1418 (1961); the figure of 50° given in this paper should read 5°.

[5] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *ibid.*, 4821 (1962).

[6] K. S. Brenner, E. O. Fischer, H. P. Fritz, and C. G. Kreiter, *Chem. Ber.*, **96**, 2632 (1963).

TABLE I

ANALYTICAL DATA

	Compound	% C Calcd	% C Found	% H Calcd	% H Found	% Cl Calcd	% Cl Found
I	$[C_8H_8RhCl]_2$	39.6	40.0	3.3	3.5	14.6	14.6
II	$[C_8H_8Rh_2Cl_2]_n$	25.2	25.4	2.1	2.3	18.6	18.6
III[a]	$C_8H_8Rh(C_5H_7O_2)$	51.0	51.2	4.9	4.6	...	...
IV[b]	$C_8H_8Rh_2(C_5H_7O_2)_2$	42.5	42.8	4.4	4.5	...	...
V	$C_8H_8RhCl(C_5H_5N)$	48.6	49.1	4.1	3.9	11.0	11.0[c]
VI	$C_8H_8Rh_2Cl_2(C_5H_5N)_2$	40.1	39.6	3.4	3.3	13.2	12.4[d]
VII	$C_8H_8RhCl(P(C_6H_5)_3)$	61.9	61.8	4.6	4.7	7.0	6.8
VIII	$C_8H_8Rh_2Cl_2(P(C_6H_5)_3)_2$	58.4	58.3	4.2	4.4	7.8	7.9

[a] Molecular weight: calcd, 306; found, 309. [b] Molecular weight: calcd, 508; found, 501. [c] % N: calcd, 4.4; found, 4.5. [d] % N: calcd, 5.2; found, 5.3.

of the complex and its decomposition was therefore undertaken.

Experimental Section

Measurements.—Infrared spectra were measured on Nujol and hexachlorobutadiene mulls using a Perkin-Elmer 337 double-beam grating spectrophotometer in the range 2000–400 cm^{-1}. Proton nmr spectra were recorded in various solvents (Table II) using approximately 1% TMS as internal standard on a Perkin-Elmer R10 60-Mc spectrometer. Microanalyses were carried out by the Microanalytical Laboratory of University College London, by Messrs. Weiler and Strauss, Oxford, and by Alfred Bernhardt, Max Planck Institut für Kohlenforschung, Mülheim, Germany. Molecular weights were determined on a Mechrolab vapor pressure osmometer, Model 301A, using approximately 0.05 *M* solutions in benzene. Analytical and molecular weight data are summarized in Table I.

TABLE II

NMR DATA FOR CYCLOOCTATETRAENE–RHODIUM COMPLEXES

Compound	Solvent	Chemical shifts[a] "Uncoordinated"	Chemical shifts[a] "Coordinated"	Coupling constants, cps, $J[^{103}Rh-^1H$(coordinated)]
C_8H_8	CS_2	4.06		
	CCl_4	4.09		
$[C_8H_8RhCl]_2$ (I)	CS_2	4.07	5.63	2.0
C_8H_8Rh(acac) (III)	CCl_4	4.04	5.78	2.0
$C_8H_8Rh_2$(acac)$_2$ (IV)	CCl_4[b]	Absent	5.25	1.0
$C_8H_8RhCl(C_5H_5N)$[c] (V)	C_5H_5N	3.91	5.43	2.2

[a] In ppm from TMS (τ 10). [b] Saturated solution. [c] A solution of complex I in pyridine gives the same spectrum.

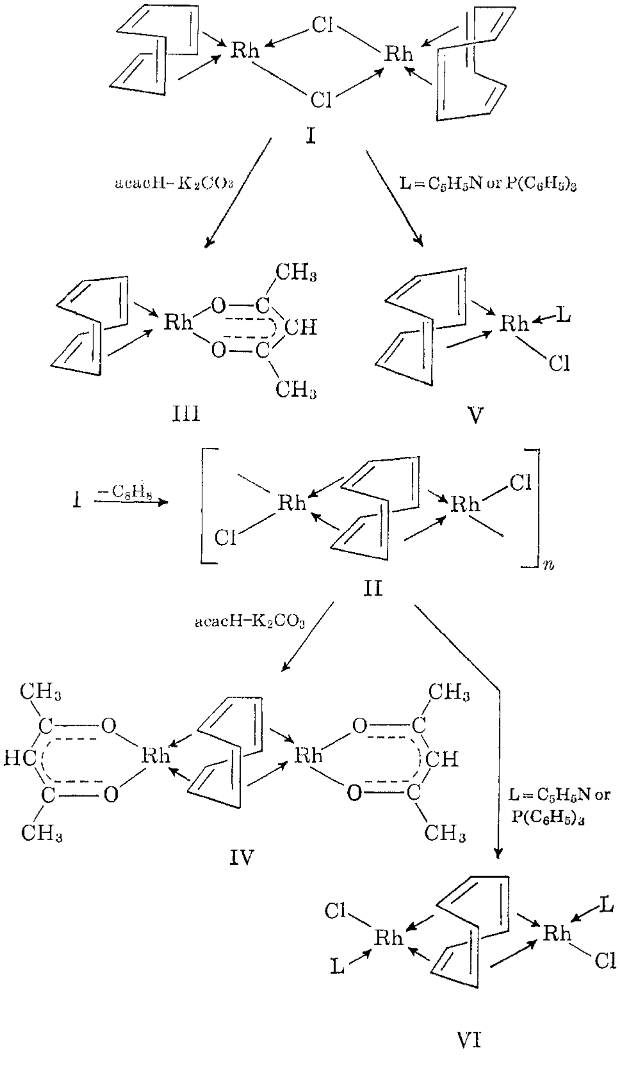
Preparation of Compounds. Di-μ-chloro-di(cyclooctatetraene)dirhodium(I), $[C_8H_8RhCl]_2$ (I).—The cyclooctene complex $(C_8H_{14})_2RhCl$ (0.5 g), prepared by the literature method,[7] was suspended in petroleum ether (bp 60–80°) and excess cyclooctatetraene (*ca.* 5 ml) added. After stirring for 1 hr at room temperature, the yellow crystalline solid was filtered, washed with alcohol and ether, and dried at 25° (0.1 mm) (yield ~85%).

Di-μ-chloro-μ-cyclooctatetraene-dirhodium(I) polymer, $[C_8H_8Rh_2Cl_2]_n$ (II).—Complex I was dissolved in chloroform and stirred at room temperature in a nitrogen atmosphere. The initially clear orange solution turned cloudy after 5 min and an orange precipitate began to form. After 1 hr, the product was filtered, washed thoroughly with alcohol and ether, and dried at 25° (0.1 mm) (yield ~65%). The same product was obtained more slowly using carbon disulfide as solvent.

2,4-Pentanedionato(cyclooctatetraene)rhodium(I), C_8H_8Rh(acac) (III).—Complex I (0.24 g) and anhydrous potassium carbonate (0.20 g) were suspended in dry petroleum ether (bp 60–80°) and treated with 2,4-pentanedione (0.2 ml). After stirring at room temperature for 1 hr, the yellow solution was filtered and solvent was evaporated from the filtrate at 25° (15 mm). Yellow crystals of III were obtained in 80% yield. After recrystallization from petroleum ether (bp 60–80°), they melted at 130°.

2,4-Pentanedionato-μ-cyclooctatetraene-dirhodium(I), $C_8H_8Rh_2$(acac)$_2$ (IV).—Complex II (0.28 g) and anhydrous potassium carbonate (0.30 g) were suspended in dry petroleum ether (bp 60–80°) and treated with 2,4-pentanedione (0.3 ml). The solution was stirred for 1 hr, and the yellow solid was filtered off. This was extracted with chloroform (three 10-ml portions) at room temperature. Evaporation of solvent from the solution at 25° (15 mm) gave orange crystals of IV in ~65% yield. After recrystallization from carbon tetrachloride, they melted at 250° dec.

Pyridine and Triphenylphosphine Complexes (V–VIII).—Com-



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[7] L. Porri, A. Lionetti, G. Allegra, and A. Immirzi, *Chem. Commun.*, 336 (1965).

TABLE III

CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES (CM^{-1}) OF CYCLOOCTATETRAENE–RHODIUM(I) COMPLEXES[a]

		ν(C=C)		Ring def	
	Compound	Uncoordinated	Coordinated	freq	Other characteristic bands
	C_8H_8	1630 m, 1605 w	. . .	1395 m, 802 s	1220 m, 1200 w, 968 w, 944 m, 672 s, br, 630 s
I	$[C_8H_8RhCl]_2$	1630 w	1410 w	1345 s, 797 s	1154 w, br, 1133 w, 987 m, 959 m, 927 m, 828 w, 816 m, 742 m, 729 w, 719 m, 603 s, 477 s
II	$[C_8H_8Rh_2Cl_2]_n$	*b*	*c*	1320 s, 811 s, br	1091 m, 959 m, 919 s, 742 w, sh, 723 m, 710 w, sh, 602 w, 534 m, 475 m
III	$C_8H_8Rh(acac)$	1630 w	*c*	1350 m, sh, 799 s	*d*
IV	$C_8H_8Rh_2(acac)_2$	*b*	*c*	1325 m, 807 s	1087 m, 540 m
V	$C_8H_8RhCl(C_5H_5N)$	1630 w	1410 w	1350 s, 800 s	*d*
VI	$C_8H_8Rh_2Cl_2(C_5H_5N)_2$	*b*	*c*	1325 s, 811 s, br	1090 m, 535 m
VII	$C_8H_8RhCl(P(C_6H_5)_3)$	1630 w	*c*	1350 m, 800 m	*d*
VIII	$C_8H_8Rh_2Cl_2(P(C_6H_5)_3)_2$	*b*	*c*	1330 m, 818 m	1094 s, 535 s

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; br, broad. [b] Not observed at or near 1630 cm^{-1}. [c] Cannot be located with certainty. [d] Bands due to cyclooctatetraene not readily distinguished from other ligand absorption.

plex I or II (0.20 g) suspended in 40 ml of petroleum ether (bp 60–80°) was treated with an approximately 10% molar excess of pyridine or triphenylphosphine and stirred for 5 hr at room temperature. The yellow products were filtered, washed thoroughly with petroleum ether, and dried at 25° (0.1 mm). The insolubility and instability of the compounds precluded attempts at recrystallization.

Results

The reaction of hydrated rhodium(III) chloride in ethanol with cyclooctatetraene usually gives a dark brown product, and we have been unable to prepare pure $[C_8H_8RhCl]_2$ by this means. However, cyclooctatetraene reacts at room temperature with the rhodium–cyclooctene complex, $(C_8H_{14})_2RhCl$,[7,8] to give the required complex as an air-stable, yellow solid. Similar displacement reactions of $(C_8H_{14})_2RhCl$ with other olefins have recently been reported.[9]

The nmr spectrum of a freshly prepared solution of I in carbon disulfide shows two broad bands of equal area (Table II), the chemical shift values being in good agreement with those reported previously for this complex,[4] despite the failure to reproduce the method of preparation. The signal at τ 4.1 is close to that of free cyclooctatetraene,[10] while the signal at τ 5.63 is a doublet (J = 2.0 cps) presumably due to ^{103}Rh–^{1}H coupling. This evidence strongly suggests that the diolefin is in a tub conformation (structure I), as suggested previously,[4] with the signal at lower field arising from equivalent protons attached to the free double bonds and the signal at higher field arising from the protons attached to the coordinated double bond. A similar value for J_{Rh-H} has been found in the complex $C_8H_8RhC_5H_5$.[5,6] The "uncoordinated" protons are probably more weakly coupled to the rhodium nucleus and spin–spin interactions between the protons themselves probably mask the expected doublet structure.

In agreement with structure I, the infrared spectrum of $[C_8H_8RhCl]_2$ shows a band at 1630 cm^{-1} assignable to a free C=C stretching frequency (Table III); a weak band at 1410 cm^{-1}, which is absent from the spectrum of cyclooctatetraene, may be due to a coordinated C=C stretching frequency. It may be noted that structure I is similar to that determined by X-rays for the rhodium(I) complex of 1,5-cyclooctadiene, $[1,5\text{-}C_8H_{12}RhCl]_2$.[11]

When a solution of $[C_8H_8RhCl]_2$ in carbon disulfide is allowed to stand, an orange-brown precipitate of formula $C_8H_8Rh_2Cl_2$ is formed, and the peak at τ 5.63 in the nmr spectrum gradually decreases in intensity while the peak at τ 4.1 becomes sharper, although its area remains constant. After some hours, only a single sharp peak at τ 4.12 remains. The orange-brown, insoluble precipitate is also formed when $[C_8H_8RhCl]_2$ is allowed to stand in chloroform, and it appears to be identical with the main product obtained from the direct reaction of rhodium(III) chloride with cyclooctatetraene. Its infrared spectrum shows no band at 1630 cm^{-1}, which suggests that all of the double bonds of the olefin are coordinated; the position of the coordinated C=C frequency cannot be located with certainty. These data and the reactions with ligands discussed below suggest that $C_8H_8Rh_2Cl_2$ may have a polymeric structure II, in which cyclooctatetraene and two chlorine atoms alternately bridge pairs of rhodium atoms, with a square-planar arrangement of ligands about the metal. The eight-membered ring is probably coordinated *via* the 1,5 and the 3,7 double bonds to different rhodium atoms. The changes in the nmr spectrum of $[C_8H_8RhCl]_2$ are evidently due to the appearance of free cyclooctatetraene as the insoluble complex $C_8H_8Rh_2Cl_2$ is formed.

Reactions of the Complexes.—The chlorine bridges of $[C_8H_8RhCl]_2$ are split by pyridine and triphenylphosphine to give complexes of formula C_8H_8RhCl(ligand) and by 2,4-pentanedione (acetylacetone, acacH) in the presence of base to give a crystalline, monomeric complex $C_8H_8Rh(acac)$. Similar reactions have been observed with the dimeric, chloro-bridged complexes of rhodium(I) with 1,5-cyclooctadiene[12] and norbornadi-

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(8) G. Winkhaus and H. Singer, *Chem. Ber.*, **99**, 3602 (1966).

(9) L. Porri and A. Lionetti, *J. Organometal. Chem.* (Amsterdam), **6**, 422 (1966).

(10) This is given incorrectly in ref 4 as τ 5.48.

(11) J. A. Ibers and R. G. Snyder, *J. Am. Chem. Soc.*, **84**, 495 (1962); *Acta Cryst.*, **15**, 923 (1962).

(12) J. Chatt and L. M. Venanzi, *Nature*, **177**, 852 (1956); *J. Chem. Soc.*, 4735 (1957).

ene.[4] The infrared spectra of these monomeric complexes show the uncoordinated C═C stretching frequency at 1630 cm^{-1}, and the pyridine complex also shows the band at 1410 cm^{-1} which may be due to the coordinated C═C stretching frequency. In addition to the signals due to the protons of the eight-membered ring (Table II), the nmr spectrum of $C_8H_8Rh(acac)$ shows sharp singlets at τ 8.02 (intensity 3) and τ 4.55 (intensity 1) arising from the methyl protons and the adjacent proton of 2,4-pentanedione. These data are consistent with structure III for the complex $C_8H_8Rh(acac)$.

The polymeric complex $C_8H_8Rh_2Cl_2$ also reacts with pyridine and triphenylphosphine giving fairly insoluble complexes of general formula $C_8H_8Rh_2Cl_2(ligand)_2$, the infrared spectra of which show no band at 1630 cm^{-1}. Reaction with 2,4-pentanedione in the presence of base gives an orange, monomeric complex of formula $C_8H_8Rh_2(acac)_2$. The nmr spectrum shows a doublet (J = 1.0 cps) at τ 5.25 (intensity 8) due to equivalent protons of the eight-membered ring, together with singlets at τ 8.13 (intensity 3) and τ 4.67 (intensity 1) due to the 2,4-pentanedione protons. This is consistent with structure IV for the complex, with tub-shaped cyclooctatetraene bridging two rhodium atoms. The value of J_{Rh-H} (1.0 cps) is very similar to that observed in the complex $C_8H_8Rh_2(C_5H_5)_2$ (J = 0.75 cps),[6] which is also believed to contain bridging cyclooctatetraene in a tub conformation. This assignment has recently been confirmed by X-ray study of the analogous cobalt compound, $C_8H_8Co_2(C_5H_5)_2$.[13]

Discussion

The location of the coordinated C═C stretching frequency in cyclooctatetraene–metal complexes is a matter of some difficulty. The following assignments of ν(C═C) (coordinated) have been made: 1431 cm^{-1} in $C_8H_8CoC_5H_5$,[14] 1525 cm^{-1} in C_8H_8CuCl and $C_8H_8 \cdot 2CuBr$,[15] 1449 cm^{-1} in $C_8H_8PdCl_2$,[14] and 1431 cm^{-1} in $C_8H_8AgNO_3$, while ν(C═C) for C_8H_8 occurs at 1635 and 1609 cm^{-1}. Since, in general, the shift of ν(C═C) on complex formation, $\Delta\nu$(C═C), falls in the order Pt(II) > Pd(II) > Cu(I) > Ag(I), the assignment in the case of the silver nitrate complex seems doubtful. In general, the shift $\Delta\nu$(C═C) is about the same for olefin complexes of rhodium(I) and platinum(II),[8,16] but, unfortunately, neither the free nor the coordinated C═C stretching frequency in $C_8H_8PtI_2$ could be located.[14] Our tentative assignment of the band at 1410 cm^{-1} in the spectra of the rhodium(I) complexes of cyclooctatetraene is at least consistent with the reported failure to observe ν(C═C) (coordinated) above 1475 cm^{-1} in the spectrum of $[1,5\text{-}C_8H_{12}RhCl]_2$;[11] in free 1,5-cyclooctadiene ν(C═C) appears at 1657 cm^{-1}.

All of the cyclooctatetraene–rhodium(I) complexes show a characteristic sharp band in their infrared spectra in the range 1300–1400 cm^{-1} and a band near 800 cm^{-1} (Table III). Similar bands in the spectrum of the free olefin have been assigned to ring deformation vibrations.[17] In $[C_8H_8RhCl]_2$ and its mononuclear derivatives, the first band appears at *ca.* 1350 cm^{-1}, but in $[C_8H_8Rh_2Cl_2]_n$, and its binuclear derivatives, it appears at *ca.* 1325 cm^{-1}. Similar features have been observed in two related series of platinum(II) complexes, $C_8H_8PtR_2$ and $C_8H_8Pt_2R_4$ (R = an alkyl or aryl group);[18,19] the mononuclear series show a strong band at 1372 cm^{-1}, which shifts to 1352 cm^{-1} in the binuclear complexes. For these platinum(II) complexes, it was noted[18,19] that the band at 800 cm^{-1} is about ten times more intense in the binuclear complexes than in the mononuclear complexes. Our rhodium(I) complexes do not show this behavior, although there are small changes in the position of the 800-cm^{-1} band (Table III).

A detailed analysis of the infrared spectra of the rhodium complexes in the region below 1300 cm^{-1} is not possible owing to the large number of bands, many of which are of course due to coordinated acetylacetone, pyridine, or triphenylphosphine. However, medium to strong bands at *ca.* 1090 and *ca.* 535 cm^{-1} seem to be characteristic of complexes containing bridging, tub-shaped cyclooctetraene. The corresponding bands in $C_8H_8Co_2(C_5H_5)_2$ appear at 1079 and 522 cm^{-1}.[14]

Attempts to recrystallize the mononuclear platinum(II) complexes $C_8H_8PtR_2$ give the binuclear complexes $C_8H_8Pt_2R_4$,[19] and the complex $C_8H_8CoC_5H_5$ decomposes in solution to $C_8H_8Co_2(C_5H_5)_2$ and C_8H_8.[20] These observations parallel the decomposition of $[C_8H_8RhCl]_2$ into $[C_8H_8Rh_2Cl_2]_n$ and C_8H_8, and of the mononuclear complexes V and VII to the binuclear complexes VI and VIII. It is not clear why the 2,4-pentanedionato complex III should be more stable to loss of cyclooctatetraene.

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(13) E. Paulus, W. Hoppe, and R. Huber, *Naturwissenschaften*, **54**, 67 (1967).

(14) H. P. Fritz and H. Keller, *Chem. Ber.*, **95**, 158 (1962).

(15) G. N. Schrauzer and S. Eichler, *ibid.*, **95**, 260 (1962).

(16) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

(17) E. R. Lippincott, R. C. Lord, and R. S. McDonald, *J. Am. Chem. Soc.*, **73**, 3370 (1951).

(18) J. R. Doyle, J. H. Hutchinson, N. C. Baenziger, and L. W. Tresselt, *ibid.*, **83**, 2768 (1961).

(19) C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, *Inorg. Chem.*, **2**, 1255 (1963).

(20) S. Otsuka and A. Nakamura, *ibid.*, **5**, 2059 (1966).