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PENTAPHENYLCYCLOPENTADIENYL CARBONYL COMPLEXES OF GROUPS VI AND VIII

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ABSTRACT

A systematic review and new approach to the syntheses of the Group VI and Group VIII transition metal derivatives of the pentaphenylcyclopentadienyl ligand are described. Significant enhancement in stability and reactivity of these perphenylated complexes is observed when compared to cyclopentadienyl and peralkylatedcyclopentadienyl derivatives due to their much higher molecular weights, reduced volatility, and modified solubility. These compounds have proved to be easily synthesized from the now readily available starting material, pentaphenylcyclopentadiene. Numerous physical and spectral properties as well as the x-ray crystal structure of a ruthenium derivative are reported.

INTRODUCTION

In spite of extensive research involving synthesis, spectroscopic characterization, and reactivity of transition metal complexes possessing one or more cyclopentadienyl or pentamethylcyclopentadienyl rings [1], relatively little work has been performed in the area of transition metal complexes incorporating an electron-depleted cyclopentadienide ligand. Recently, interest in such groups has been kindled by papers reporting complexes of cyclopentadienyls incorporating the trifluoromethyl group [2] and the percarbomethoxycyclopentadienyl group [3]. Electrochemical studies have characterized the pentaphenylcyclopentadienide ligand as falling in this class, the ligand affording considerable enhancement of kinetic stability as well as oxidative stability to appropriate complexes [4].

No systematic synthesis of complexes of this ligand has been reported, although several examples are known. Organic starting materials for individual syntheses of transition metal derivatives include diphenylacetylene [5, 6], Ph_5C_4Al [7], PH_5C_5Br [8, 9], the Ph_5C_5 radical [10], PH_5C_5Na [11, 12], and Ph_5C_5H [12].

Of the known complexes, three have been characterized via x-ray studies: transition metal dinuclear complexes of Pd [11] and Ni [10], and the dicarbonylcobalt complex [12], evidently examined while this work was in progress. Other complexes of relevant interest include a bis complex of iron and other transition metals and the tetraphenylcyclopentadienide ligand [9, 13, 14] and the main-group element C_5Ph_5 sandwiches of tin [15]. Isolation of this latter complex serves as a persuasive argument for the ligand's contribution to the kinetic and thermodynamic stability of the overall complex. Theoretical justification of its VSEPR-disobeying geometry has now been adduced [16].

Our large-scale synthesis and detailed characterization of pentaphenylcyclopentadiene [17] provided us with a strong starting point for entry into more systematic preparative studies of C_5Ph_5 and its transition metal complexes [18]. Indeed, reflecting our continuing interest in cyclopentadienyl complexes of Group VI [19], we have prepared a series of new pentaphenylcyclopentadienyl complexes of chromium, molybdenum, and tungsten as illustrated in Eq. (1). Treatment of colorless solutions of $C_5Ph_5^-L^+$ [20] with $M(CO)_6$, where M = Cr, Mo, or W, in diglyme, THF, or glyme, respectively, produced the corresponding yellow lithium salts *1*, *2*, and *3*.

These were isolated in high yields (up to 90%) as yellow, stable, but very air-sensitive solids and were characterized. Treatment of *2* and *3* with excess iodomethane in THF or glyme at reflux afforded the yellow, air-stable σ-methyl derivatives, *4* and *5*, in yields of ∿80%.

$$C_5Ph_5Li^+ + M(CO)_6 \longrightarrow \begin{array}{l} [C_5Ph_5M(CO)_3]^-Li^+ \\ \mathit{1}, M = Cr \\ \mathit{2}, M = Mo \\ \mathit{3}, M = W \end{array}$$

$$\xrightarrow{CH_3I} \begin{array}{l} C_5Ph_5M(CO)_3CH_3 \\ \mathit{4}, M = Mo \\ \mathit{5}, M = W \end{array} \qquad (1)$$

The first structural characterization of a dicarbonyl bromide complex of a transition metal containing the pentaphenylcyclopentadienyl ring has also been accomplished. η^5-Pentaphenylcyclopentadienylruthenium dicarbonyl bromide (*6*) was synthesized, under argon, from $Ru_3(CO)_{12}$ and bromopentaphenylcyclopentadiene according to

$$3C_5Ph_5Br + Ru_3(CO)_{12} \xrightarrow{\Delta} \underset{\mathit{6}}{3C_5Ph_5Ru(CO)_2Br} + 6CO \qquad (2)$$

The orange, air-stable product was purified by elution through a silica gel column with dichloromethane and precipitation with hexane. The ^{13}C- and ^1H-NMR spectra clearly show the formation of monomeric species containing the η^5-pentaphenylcyclopentadienyl group and the carbonyl ligands. Microanalysis of the material establishes it as $C_{37}H_{25}BrO_2Ru$. Molecular weights calculated for formulas $^{12}C_{37}H_{25}{}^{16}O_2{}^{102}Ru^{79}Br$ and $^{12}C_{37}H_{25}{}^{16}O_2{}^{102}Ru^{81}Br$ are 682 and 684, respectively; indeed, two peaks at m/e = 682 and 684 are the most intense in the compound's mass spectrum.

The molecular weight as determined by vapor pressure osmometry ($CHCl_3$ as a solvent) is 674 amu. The IR spectrum is fully consistent with the proposed formula and shows classical very strong ν(CO) bands at 2035 and 1985 cm^{-1} as well as aromatic ν(CH) bands at 3030 cm^{-1}.

Single crystals, suitable for x-ray diffraction studies, were grown by slow interdiffusion of heptane placed on top of a dichloromethane solution of *6*. A view of the molecule as seen from the top of the dicarbonyl bromide moiety is presented in Fig. 1. Intensity data were collected on a CAD-4 single-crystal diffractometer. All the nonhydrogen atoms were

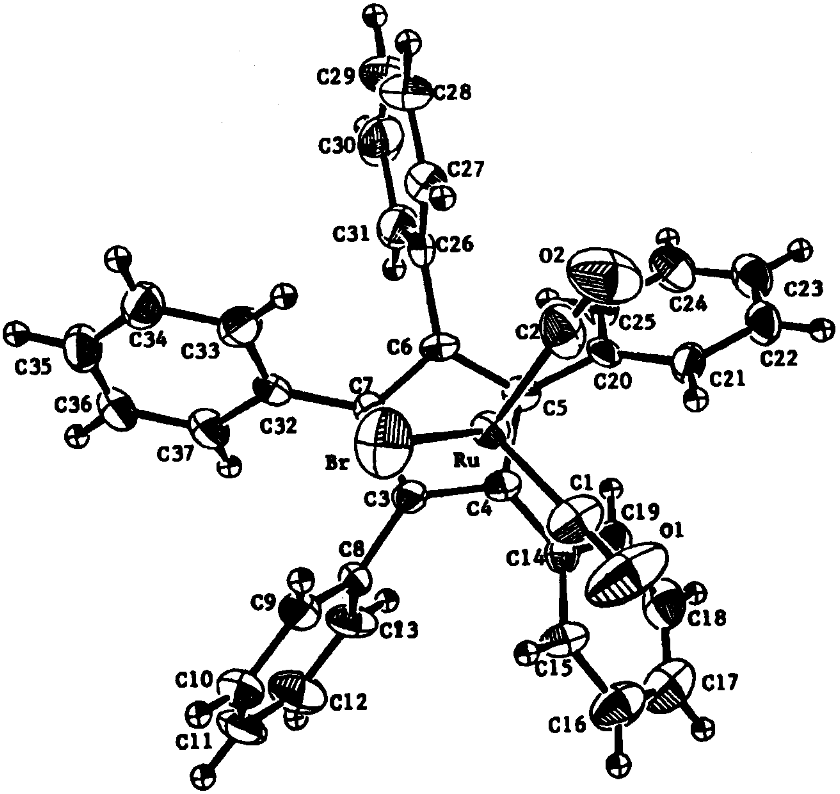

FIG. 1.

refined anisotopically. The hydrogen atoms were added to phenyl rings at calculated distances with a thermal parameter $B = 5.0$ Å^2; this was included in the structure factor calculation but not refined. Basic information concerning the cell parameters and crystallographic analysis are summarized in Table 1.

The x-ray study of *6* fully confirms the η^5-bonding mode of the bulky

TABLE 1. Crystallographic Data for $(\eta^5\text{-}C_5Ph_5)Ru(CO)_2Br$

Formula	$RuBrO_2C_{37}H_{25}$
Formula weight	682.59
Space group:	P_{bca}
a, Å	21.738(6)
b, Å	18.042(6)
c, Å	14.971(6)
V, Å^3	5871.1 Å^3
Z	8
d_{calc}, g/cm^3	1.544
Crystal size, mm	0.25 × 0.30 × 0.20
Data collection instrument	Enraf-Nonius CAD-4
Radiation (monochromated in incident beam)	MoK$_\alpha$ ($\lambda = 0.71073$ Å)
Orientation reflections, number, range (2θ)	24, 4–16
Temperature, °C	22
Scan method	$\theta - \omega$
Data col. range, 2θ, deg.	$0 < 2\theta < 50$
No. unique data, total with $F_0^2 > 3\sigma(F_0^2)$	6732 2573
Number of parameters refined by full-matrix least-squares refinements	370
Trans. factors, max., min.	min 94.24; max 99.8; ave 96.11
R^a	0.040
$R_w{}^b$	0.045
Quality-of-fit indicator^c	1.2
Largest shift/esd, final cycle	0.39
Largest peak, e/Å^3	0.398

[a] $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$.

[b] $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$; $w = 1/\sigma^2(|F_0|)$.

[c] Quality of fit $= [\Sigma w(|F_0| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

C_5Ph_5 ligand to the ruthenium atom. The compound has the piano-stool structure, i.e., the coordination sphere of the ruthenium atom can be regarded as a distorted octahedron with the bulky C_5Ph_5 ligand occupying three coordination sites. The most important internuclear distances and angles (Table 2) correspond to this structure type and are well within the range observed in bis(cyclopentadienyldicarbonylruthenium) [21] and $C_5Me_4EtRu(CO)_2Br$ [22], which may be considered as the closest structurally characterized congeners.

The most distinctive structure feature of *6* is the paddlewheel arrangement of the five phenyl substituents which are canted relative to the cyclopentadienyl ring. The five dihedral angles between the cyclopentadienyl plane and the five planes, each involving a different phenyl ring, are 60.2, 39.3, 62.0, 92.6, and 51.9°, respectively, and suggest clearly severe steric crowding caused by the five phenyl groups, as expected. This is in modest contrast to the results recently obtained for the complex $C_5Ph_5Co(CO)_2$, wherein the same five dihedral angles are reported to range only from 50.4 to 68.2°.

The above results show that the C_5Ph_5 ligand can be conveniently handled and utilized for preparation of a large variety of novel, transition metal complexes possessing high molecular weights and containing a very sterically demanding ligand.

EXPERIMENTAL

Pentaphenylcyclopentadiene-1-ol

A 3-L flask equipped with a condenser, large dropping funnel, and a magnetic stirrer was charged with 103 g tetracyclone and 1 L reagent-grade benzene which had been dried over Na benzophenone. Stirring was continued until the contents of the flask dissolved. Phenylmagnesium bromide, prepared from 13.0 g (0.54 mol) magnesium shavings and 57 mL (0.54 mol) bromobenzene in 300 mL anhydrous ether, was filtered into the dropping funnel and was slowly added to the stirred reaction mixture. After about three-quarters of the Grignard reagent was added, the reaction mixture turned and remained light brown. The final mixture was refluxed for 2 h, cooled, and hydrolyzed with 1.5 L of a 10% ammonium chloride solution. The organic layer was separated, washed twice with 200 mL portions of water, and dried over anhydrous magnesium sulfate. The solution was concentrated somewhat on a rotary evaporator until 300–400 mL of a viscous liquid remained. With vigorous stirring,

TABLE 2. Important Distances (Å) and Angles (degrees) for *6* in the Crystal

Ru-Br	2.537(1)	C3-C4	1.442(9)
Ru-C1	1.902(9)	C4-C5	1.451(9)
Ru-C2	1.930(9)	C5-C6	1.440(9)
Ru-C3	2.267(6)	C6-C7	1.411(8)
Ru-C4	2.239(6)	C7-C3	1.462(9)
Ru-C5	2.215(6)	C3-C8	1.484(9)
Ru-C6	2.265(6)	C4-C14	1.481(9)
Ru-C7	2.304(6)	C5-C20	1.480(9)
O1-C1	1.102(8)	C6-C26	1.510(9)
O2-C2	1.024(8)	C7-C32	1.469(9)
Br-Ru-C1	86.8(2)	C4-C5-C6	107.4(6)
Br-Ru-C2	85.5(3)	C5-C6-C7	109.5(6)
C1-Ru-C2	87.9(3)	C6-C7-C3	107.7(6)
C3-C4-C5	107.7(6)	C7-C3-C4	107.7(6)

2.5 L hexane was added to the solution, causing the alcohol to precipitate. The slurry was isolated on a Büchner funnel, washed with hexane, and dried overnight in an oven set at 100°C. The yield was 102 g (82%) of a yellowish white solid manifesting a very strong fluorescence in the UV, mp 176–177°C (literature mp 176–178°C [12]). The alcohol was not recrystallized before further use.

Bromopentaphenylcyclopentadiene [23]

A 1-L flask was charged with 30.0 g (0.065 mol) pentaphenylcyclopentadiene-1-ol, 300 mL glacial acetic acid and 60 g of a 12.5% solution of HBr in acetic acid. The reaction mixture was stirred at room temperature for 0.5 h followed by reflux for 1 h. After cooling, 100 mL petroleum ether was added and the resulting slurry filtered. The solid residue was washed with acetic acid followed by methanol and then vacuum dried. The yield was 31.0 g (90%) of an orange solid, mp 188°C (literature mp 188–189°C [24]). A mass spectrum of this compound exhibits two parent peaks at m/e's of 524 and 526 due to the molecules possessing the two isotopes of bromine, ^{79}Br and ^{81}Br, respectively.

Pentaphenylcyclopentadienylruthenium Dicarbonyl Bromide (6) [25]

A 500-mL two-neck round-bottom flask was filled with a Teflon-coated stirring bar, a rubber septum, and a condenser equipped with an argon inlet, and the entire system was placed on a magnetic stirrer located in a well-ventilated hood. The flask was charged under an argon atmosphere with 5.0 g (7.8 mmol) $Ru_3(CO)_{12}$ (Strem Chemical), 12.46 g (23.5 mmol) bromopentaphenylcyclopentadiene, and 200 mL water and oxygen-free benzene. With slow heating the reaction began, the color of the mixture changing from orange to deep violet. Incipient gas evolution can be noted at this point. Moderate reflux was continued for 2.5 h. After the system had cooled, the benzene solution was concentrated to a volume of 50 mL under vacuum. The resulting slurry was isolated on a Büchner; exposure to air changed the color of the compound from violet to orange. The solid residue was washed with hexane and dried under vacuum.

The product was purified by dissolution in dichloromethane followed by filtration through a 20 × 2 cm silica gel column (E. Merck Silica Gel 60). An equal volume of hexane was added to the orange solution. Slow concentration of this solution on a rotary evaporator eventually brought about crystallization. Vacuum filtration afforded an orange crystalline product that was vacuum dried; yield 11.5 g (66%), mp > 200°C. The complex is soluble in benzene, dichloromethane, and THF, but the solutions decompose slowly even in the absence of air. ^1H NMR ($CDCl_3$); 7.1 (m), ^{13}C NMR ($CDCl_3$); 196.6(s)(CO), 132.3, 129.6, 128.4, 127.8 (Ph's), 106.4 (s) (C_5 ring), IR(KBr); 2035, 1985 cm^{-1} (νCO).

SUPPLEMENTARY MATERIALS AVAILABLE

List of fractional atomic positional parameters, thermal parameters, bond length and angle data, details of the crystallographic experimental procedures (6 pages), and tables of observed and calculated structure factors, amplitudes (29 pages).

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