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Synthesis and Properties of Rhodium(I) Chloranilate and 2,5-Dihydroxy-1,4-benzoquinonate Complexes. Crystal Structures of the Binuclear [Rh$_2$(μ-CA)(cod)$_2$] and Tetranuclear [Rh$_4$(μ-CA)$_2$(cod)$_4$] Complexes (CA = Chloranilate Anion)

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If one treats [Rh$_2$(μ-OMe)$_2$(diolefin)$_2$] {diolefin = cycloocta-1,5-diene (cod), norborna-1,5-diene (nbd) or tetrafluoro-[5,6]bicyclo[2.2.2]octa-2,5,7-triene (tfb)} with chloranilic acid (H$_2$CA) or 2,5-dihydroxy-1,4-benzoquinone (H$_2$-DHBQ) in a 1:1 ratio, the binuclear complexes [Rh$_2$(μ-L)(diolefin)$_2$] (L = CA^{2-}, DHBQ^{2-}) can be obtained. The complex [Rh(acac)(cod)] (acac = acetylacetonate) reacts with H$_2$CA to give the tetranuclear complex [Rh$_4$(μ-CA)$_2$(cod)$_4$]. The complex [Rh$_2$(μ-DHBQ)(cod)$_2$] undergoes two sequential reversible one-electron reductions at a platinum electrode in dichloromethane. The crystal structures of the complexes Rh$_4$(μ-CA)$_2$(cod)$_4$] (**1**) and [Rh$_2$(μ-CA)(cod)$_2$] (**2**) have been determined by X-ray diffraction methods. Crystal data for **1**: space group $P2_1/n$, a = 15.284 (6) Å, b = 8.976 (4) Å, c = 16.553 (7) Å, β = 112.40 (2)°, Z = 2, 2086 reflections, R = 0.0253. Crystal data for **2**: space group $C2/c$, a = 19.310 (7) Å, b = 6.608 (3) Å, c = 19.283 (8) Å, β = 117.06 (2)°, Z = 4, 1526 reflections, R = 0.0624. In the centrosymmetric tetranuclear complex **1** each CA^{2-} dianion, in the o-quinone form, displays a novel coordination mode interacting with three rhodium atoms via three σ-bonds through oxygens and two π-bonds through two adjacent double bonds. The coordination around each Rh atom is completed by a cod molecule interacting in the usual manner through the two double bonds. If the midpoints of the double bonds interacting with the metals of the CA^{2-} and cod ligands are taken into account, two Rh atoms are in a square planar and two are in a square pyramidal arrangement. The CA^{2-} ligand, involved in a very complicate bonding with three metals, has lost the planarity, the six-membered ring showing a "boat" conformation with the two planar moieties tilted by 31.6 (3)°. In the centrosymmetric binuclear complex **2**, the strictly planar CA^{2-} ligand, in the more common p-quinone form, chelates to two Rh centers through the oxygen atoms as a tetradentate ligand. The coordination around each Rh atom is completed by a cod ligand.

Introduction

Several recent publications have established that the coordination compounds of quinones display many interesting features, among them, their rich redox chemistry. These ligands can be bound to the metal ions in three different oxidation states: quinone,[1] semiquinone[2] or catechol, and hydroquinone,[3] and they have shown ability to undergo intramolecular interligand[4] or metal–ligand[5] electron transfer reactions. In this context, relatively few transition-metal coordination compounds of 2,5-dihydroxy-1,4-benzoquinone (H$_2$DHBQ) and its chloro derivative, chloranilic acid (H$_2$CA), have been reported. They can be considered as stabilized enols of 1,2-diketonates; therefore, they facilitate the substitution of the enolic hydrogen by a metal ion.[6] First-row transition-metal complexes that have appeared in the literature include 1:1 coordination polymers,[7] Ni(II),[8] Cu(II),[8,9] and Fe(III)[7a,10] binuclear complexes, and Cr(III) complexes which serve as ethanol oxidation catalysts under mild conditions.[11] Zubieta et al.[12] recently reported the structures for some

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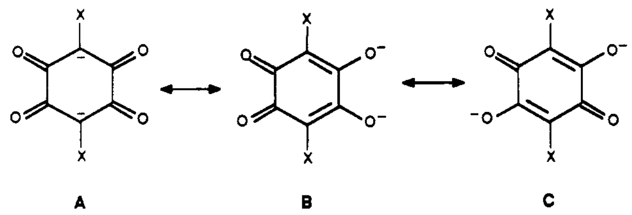

Figure 1. Resonance forms of $DHBQ^{2-}$ (X = H) and CA^{2-} (X = Cl) dianions: (A) bis(carbanion); (B) *o*-quinone; (C) *p*-quinone.

polyoxomolybdate derivatives. In addition, a polymeric three dimensional network of $[Pr_2(CA)_3]\cdot 8EtOH$ has been also reported.[13]

One of the three resonance forms of these dianions (C, Figure 1), the *p*-quinone form, is present in most of the compounds described above where it chelates to the metal centers through 1,2- and 4,5-oxygen atoms. However, in the mononuclear complex $[Cu(CA)(terpy)]\cdot H_2O$[9b] (terpy = 2,2′:6′,2″-Terpyridine) is the *o*-quinone form which is present, chelating through 1,2-oxygen atoms (B, Figure 1). The bis(carbanion) form (A, Figure 1) appears in complexes of metal ions with remarkable affinity for sp^3-hybridized carbons as Pd(II)[14] or Pt(II),[15] and the isomerization of the mononuclear complex $[Pd(C\text{-}CA)(CH_3CN)_2]$ into $[Pd(\pi\text{-}CA)(PR_3)_2]$ by addition of PR_3 ligands provides a chemical model relevant to the oxidation of ethanol over Pd catalyst.[16]

As far as we know, only one π-bound quinone complex has been previously reported.[2h] This survey on the literature reveals the ability of these dianions to act as good ligands coupling the ligating ability of these enols to the redox properties of the quinone system.

In situations where both metal and ligands are redox active a large number of redox processes may be expected, and it seems interesting to extend our previous work on bi- and polynuclear rhodium complexes[17,18] with binucleating ligands, to the potentially "noninnocent" binucleating ligands H_2DHBQ or H_2CA.

In this paper, we report the synthesis and characterization of a tetranuclear Rh(I) complex and several binuclear Rh(I) complexes bridged by the $DHBQ^{2-}$ or CA^{2-}-dianions as well as the X-ray structures of $[Rh_4(\mu\text{-}CA)_2(cod)_4]$ (**1**) and $[Rh_2(\mu\text{-}CA)(cod)_2]$ (**2**). As far as we know, it is the first time that a structure of a metal-chloranilate complex, involving the *o*-quinone olefinic π-electron system, has been reported.

Experimental Section

Starting Materials and Physical Methods. The chemicals were of reagent grade and were used without further purification. Standard literature procedures were used to prepare the starting materials $[Rh(acac)(diolefin)]$ (diolefin = cod,[19] nbd,[19] tfb[20]) and $[Rh_2(\mu\text{-}OMe)_2(diolefin)_2]$ (diolefin = cod,[21] nbd,[21] tfb[22]). All solvents were dried and distilled before use by standard methods. Carbon and hydrogen analyses were performed in a Perkin-Elmer 240 B microanalyzer. IR spectra were recorded with a Perkin-Elmer 783 (4000–200 cm^{-1}) spectrophotometer as pressed potassium bromide pellets. The infrared peaks of the complexes were calibrated against the sharp peak (1601.4 cm^{-1}) of polystyrene film. UV–visible spectra were obtained by using a Hitachi Model U-3400 (800–200-nm) spectrophotometer. Samples were dissolved in methylene chloride, and spectra were taken in 1-cm path length quartz optical cells. NMR spectra were carried out in $CDCl_3$ solution at room temperature on a Varian XL 200 spectrometer. ^1H and $^{13}C\{^1H\}$ chemical shifts are referenced to $SiMe_4$ as internal standard.

Electrochemical experiments were performed with a EG&G Research Model 273 potentiostat/galvanostat. The data were passed to a IBM PS/2 computer where the curves were plotted and measured, after which the applicable calculations were performed. A three-electrode glass cell consisting of a platinum-disk working electrode, a platinum-wire auxiliary electrode and a commercial KCl saturated calomel (Tacussel) reference electrode was employed. Linear voltamperometry was performed by using a rotating platinum electrode (RDE) as the working electrode. The electrochemical experiments were performed under nitrogen atmosphere. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was recrystallized from ethanol, dried under vacuum, and used as the supporting electrolyte. Reagent grade dichloromethane was refluxed over CaH_2 for several hours and then fractionally distilled. The supporting electrolite solution was scanned over the solvent window to ensure the absence of electroactives impurities. In all measurements the sample solutions were 5×10^{-4} mol/L in complex and 0.2 mol/L in TBAH and were bubbled with nitrogen gas for 15 min to remove the O_2 prior to measurement. Under these conditions, $E°$ for the couple $[Fe(\eta\text{-}C_5H_5)_2]^+/[Fe(\eta\text{-}C_5H_5)_2]$ is 474 mV.

Preparation of Complexes. $[Rh_4(\mu\text{-}CA)_2(cod)_4]$ (1). A diethyl ether solution (25 mL) of $[Rh(acac)(cod)]$ (186 mg, 0.6 mmol) was allowed to diffuse into a solution, in the same solvent (25 mL), of H_2CA (63 mg, 0.3 mmol). After 3 days of diffusion, dark red crystals, suitable for diffraction studies, were formed at the porous frit of the H-tube; they were decanted, washed with cold diethyl ether, and dried in vacuo. Yield: 117 mg (62%). Anal. Calcd for $C_{44}H_{48}Cl_4O_8Rh_4$: C, 42.00; H, 3.81. Found: C, 42.09; H, 3.70. IR (cm^{-1}): 1692 (s), 1620 (s), 1420 (vs), 862 (m), 500 (m). UV–vis (λ_{max}, nm): 230, 330, 445. ^1H NMR (δ, Hz): 4.37 (s, 8H, HC=), 2.47 (m, 8H, H_2C—), 1.81 (d, J = 8 Hz, 8H, H_2C—).

$[Rh_2(\mu\text{-}CA)(cod)_2]$ (2). To a solution of 150 mg (0.3 mmol) of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 15 mL of diethyl ether was added with stirring a solution of 63 mg (0.3 mmol) of H_2CA in 10 mL of diethyl ether. The resultant deep brown solution was loosely stoppered and kept undisturbed at 20 °C for 24 h. The precipitate thus obtained was collected by filtration to give 70 mg of (**2**) as dark brown needles that were suitable for X-ray single-crystal analysis. The filtrate was reduced in volume, pentane (10 mL) added, and the resulting precipitate collected to give an additional 100 mg of **2**. Total yield: 170 mg (90%). Anal. Calcd for $C_{22}H_{24}Cl_2O_4Rh_2$: C, 42.00; H, 3.81. Found: C, 42.18; H, 4.03. IR (cm^{-1}): 1500 (vs), 1370 (s), 859 (m), 504 (m). UV–vis (λ_{max}, nm): 230, 330, 445. ^1H NMR (δ, Hz): 4.37 (s, 8H, HC=), 2.47 (m, 8H, H_2C—), 1.81 (d, J = 8 Hz, 8H, H_2C—).

$[Rh_2(\mu\text{-}CA)(nbd)_2]$ (3). To an acetone solution (15 mL) containing $[Rh(acac)(nbd)]$ (169 mg, 0.6 mmol) was added 63 mg (0.3 mmol) of H_2CA. A brown microcrystalline precipitate slowly separated. After this was stirred for 1 h, the resulting suspension was concentrated to ca. 5 mL and diethyl ether (10 mL) added. The microcrystalline solid was isolated by filtration, washed with cold diethyl ether, and dried in vacuo. Yield: 156 mg (91%). Anal. Calcd for $C_{20}H_{16}Cl_2O_4Rh_2$: C, 40.23; H, 2.70. Found: C, 40.48; H, 2.77. IR (cm^{-1}): 1500 (vs), 1374 (s), 855 (m), 497 (m). UV–vis (λ_{max}, nm): 230, 330, 425. ^1H NMR (δ, Hz): 4.10 (s, 8H, HC=), 3.95 (s, 4H, HC—), 1.25 (s, 4H, H_2C—). This compound was likewise prepared from $[Rh_2(\mu\text{-}OMe)_2(nbd)_2]$ (128 mg, 0.3 mmol) and H_2CA (63 mg, 0.3 mmol) by the method described for **2**. Yield: 53 mg, (31%).

$[Rh_2(\mu\text{-}CA)(tfb)_2]$ (4). A solution of H_2CA (31.5 mg, 0.15 mmol) in 10 mL of acetone was added to a solution of $[Rh(acac)(tfb)]$ (128 mg, 0.3 mmol) in 15 mL of acetone. The yellow solution quickly turned to brown, and a dark brown microcrystalline precipitate began to form almost immediately. The mixture was stirred for 1 h and was maintained at −20 °C overnight. The black microcrystalline product was collected by filtration, washed with 10 mL of cold acetone, and dried in vacuo. Yield:

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Table I. Crystallographic Data for Compounds **1** and **2**

	1	**2**
mol formula	$C_{44}H_{48}Cl_4O_8Rh_4$	$C_{22}H_{24}Cl_2O_4Rh_2$
mol wt	1258.29	629.15
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
a/Å	15.284 (6)	19.310 (7)
b/Å	8.976 (4)	6.608 (3)
c/Å	16.553 (7)	19.283 (8)
β/deg	112.40 (2)	117.06 (2)
V/Å^3	2100 (2)	2191 (2)
Z	2	4
T/°C	22	22
λ/Å	0.710 73	1.541 78
ρ_{calcd}/g cm^{-3}	1.990	1.907
μ/cm^{-1}	18.32	150.12
R^a	0.0253	0.0624
$R_w{}^b$	0.0323	0.0631

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

105 mg (81%). Anal. Calcd for $C_{30}H_{12}Cl_2F_8O_4Rh_2$: C, 41.65; H, 1.40. Found: C, 41.80; H, 1.60. IR (cm^{-1}): 1500 (vs), 1380 (s), 860 (m), 520 (m). The low solubility of this complex prevented the determination of its UV-visible and ^{1}H NMR spectra.

[Rh$_2$(μ-DHBQ)(cod)$_2$] (5). The addition of a 5-mL acetone solution of 42 mg (0.3 mmol) of H_2DHBQ to a stirred 15-mL acetone solution of [Rh(acac)(cod)] (186 mg, 0.6 mmol) results in a immediate color change from yellow to deep reddish brown. When the resulting solution was allowed to stand overnight at -20 °C, dark needle-shaped crystals were obtained, which were collected by filtration, washed with a small quantity of cold acetone, and dried in vacuo. Yield: 73 mg (43%). Anal. Calcd for $C_{22}H_{26}O_4Rh_2$: C, 47.16; H, 4.68. Found: C, 47.25; H, 4.83. IR (cm^{-1}): 3105 (m), 1520 (vs), 1385 (s), 505 (m). UV-vis (λ$_{max}$, nm): 230, 306, 427. ^{1}H NMR (δ, Hz): 5.23 (s, 2H, DHBQ), 4.21 (s, 8H, HC=), 2.47 (m, 8H, H_2C—), 1.78 (d, J = 8 Hz, 8H, H_2C—). This compound was obtained similarly from [Rh$_2$(μ-OMe)$_2$(cod)$_2$] (150 mg, 0.3 mmol) and H_2DHBQ (42 mg, 0.3 mmol) as a brown microcrystalline solid. Yield: 144 mg (85%).

[Rh$_2$(μ-DHBQ)(nbd)$_2$] (6) was prepared from [Rh(acac)(nbd)] (169 mg, 0.6 mmol) and H_2DHBQ (42 mg, 0.3 mmol) by the method described above for **3**. Yield: 115 mg (76%). It was alternatively prepared from [Rh$_2$(μ-OMe)$_2$(nbd)$_2$] (128 mg, 0.3 mmol) and H_2DHBQ (42 mg, 0.3 mmol) by a method analogous to that described for **3**. Yield: 106 mg (70%). Anal. Calcd for $C_{20}H_{18}O_4Rh_2$: C, 45.48; H, 3.05. Found: C, 45.88; H, 3.27. IR (cm^{-1}): 3110 (m), 1520 (vs), 1370 (s), 505 (m). UV-vis (λ$_{max}$, nm): 230, 306, 410. ^{1}H NMR (δ, Hz): 5.13 (s, 2H, DHBQ), 3.96 (s, 8H, HC=), 3.88 (m, 4H, HC—), 1.17 (s, 4H, H_2C—).

[Rh$_2$(μ-DHBQ)(tfb)$_2$] (7) was prepared from [Rh(acac)(tfb)] (128 mg, 0.3 mmol) and H_2DHBQ (21 mg, 0.15 mmol) by the method described above for **4**. Yield: 81 mg (68%). Anal. Calcd for $C_{30}H_{14}F_8O_4Rh_2$: C, 45.25; H, 1.77. Found: C, 45.41; H, 1.90. IR (cm^{-1}): 3105 (m), 1520 (vs), 1380 (s), 520 (m). UV-vis (λ$_{max}$, nm): 227, 282, 412. ^{1}H NMR (δ, Hz): 5.19 (s, 2H, DHBQ), 5.65 (s, 4H, HC—), 3.80 (s, 8H, HC=).

Crystal Structure Determinations of Complexes 1 and 2. Selected crystallographic data for both compounds are listed in Table I. Data were collected at room temperature on Enraf-Nonius CAD-4 (**1**) and Siemens AED (**2**) single-crystal diffractometers using graphite-monochromated Mo Kα (**1**) and nickel-filtered Cu Kα (**2**) radiations. All reflections with θ in the range 3–25° (**1**) and 3–70° (**2**) were measured; of 4058 (**1**) and 4675 (**2**) independent reflections, 2086 (**1**), having $I > 3\sigma(I)$, and 1526 (**2**), having $I > 2\sigma(I)$, were considered observed and used in the analyses. A correction for the absorption effects was applied only to the data of **2** (maximum and minimum transmission factors values were 1.568 and 0.638).[23]

Both structures were solved by Patterson and Fourier methods, and refined by full-matrix least-squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. All hydrogen atoms of **1**, excepting three, were clearly localized in the final ΔF map and refined isotropically; three hydrogen atoms of **1** and all those of **2** were placed at their calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 358 (**1**) and 148 (**2**) variables; after the last cycles, no parameters shifted by more than 1.3 (**1**) and 0.9 (**2**) esd. The highest remaining peak in the final difference map was equivalent to about 0.7 (**1**) and 1.1 (**2**) e/Å^3. A weighting scheme $w = K[\sigma^2(F_o) + gF_o{}^2]^{-1}$ was used in the last cycles of refinement of **1** with K = 0.608 and g = 0.0052 at convergence; unit weights were used in all stages of the refinement of **2**. Final R and R_W values were 0.0253 and 0.0323 (**1**) and 0.0624 and 0.0631 (**2**), respectively. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref 24. The SHELX-76 and SHELXS-86 systems of computer programs were used.[25] Final atomic coordinates for the non-hydrogen atoms are given in Tables II (**1**) and III (**2**). All calculations were carried out on the CRAY X-MP/48 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the Gould

Table II. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of [Rh$_4$(μ-CA)(cod)$_4$] (**1**)

	x/a	y/b	z/c	$U_{eq}{}^a$
Rh(1)	1595 (1)	1564 (1)	199 (1)	203 (2)
Rh(2)	3172 (1)	1545 (1)	−1506 (1)	253 (2)
Cl(1)	2904 (1)	−1705 (2)	879 (1)	357 (6)
Cl(2)	−263 (1)	2071 (2)	−1865 (1)	357 (6)
O(1)	3100 (3)	72 (5)	−564 (3)	299 (18)
O(2)	1725 (3)	1772 (5)	−1740 (3)	277 (17)
O(3)	−561 (3)	−631 (5)	−972 (3)	304 (18)
O(4)	865 (4)	−2464 (6)	131 (4)	445 (25)
C(1)	611 (4)	954 (7)	−1122 (4)	228 (25)
C(2)	1525 (4)	983 (7)	−1192 (4)	230 (21)
C(3)	2266 (4)	70 (7)	−555 (4)	223 (24)
C(4)	2010 (4)	−714 (7)	82 (4)	238 (24)
C(5)	1048 (5)	−1334 (7)	−177 (4)	279 (26)
C(6)	270 (4)	−363 (7)	−809 (4)	240 (24)
C(7)	1155 (6)	3890 (8)	356 (6)	339 (31)
C(8)	1636 (6)	3935 (8)	−200 (6)	347 (31)
C(9)	2643 (6)	4333 (10)	19 (6)	479 (35)
C(10)	3332 (6)	3682 (11)	833 (7)	562 (37)
C(11)	3064 (5)	2170 (9)	1062 (5)	323 (26)
C(12)	2543 (5)	1952 (9)	1558 (4)	318 (24)
C(13)	2119 (7)	3132 (11)	1930 (6)	506 (40)
C(14)	1588 (8)	4337 (10)	1299 (6)	522 (39)
C(15)	3239 (5)	3601 (8)	−2078 (5)	350 (29)
C(16)	3135 (6)	2482 (9)	−2685 (5)	369 (29)
C(17)	3929 (8)	1931 (12)	−2929 (7)	594 (48)
C(18)	4478 (7)	690 (13)	−2380 (6)	552 (43)
C(19)	4452 (5)	647 (10)	−1484 (5)	331 (29)
C(20)	4652 (4)	1834 (8)	−894 (5)	366 (29)
C(21)	4958 (6)	3364 (10)	−1079 (7)	522 (37)
C(22)	4149 (6)	4383 (10)	−1547 (7)	498 (38)

[a] Equivalent Isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of [Rh$_2$(μ-CA)(cod)$_2$] (**2**)

	x/a	y/b	z/c	$U_{eq}{}^a$
Rh	1492 (1)	700 (1)	1276 (1)	427 (3)
Cl	1429 (2)	6399 (4)	−492 (2)	646 (15)
O(2)	1514 (4)	3168 (11)	609 (4)	466 (31)
O(1)	2387 (4)	−165 (12)	1005 (4)	534 (30)
C(1)	2471 (5)	1055 (16)	531 (6)	432 (41)
C(2)	1957 (5)	2926 (15)	299 (5)	380 (37)
C(3)	2017 (5)	4286 (16)	−215 (5)	434 (38)
C(4)	381 (6)	1382 (16)	1126 (7)	524 (55)
C(5)	926 (6)	2142 (19)	1839 (7)	556 (55)
C(6)	1116 (8)	1248 (27)	2605 (7)	810 (65)
C(7)	1607 (12)	−663 (30)	2802 (10)	1131 (120)
C(8)	1750 (8)	−1394 (23)	2209 (8)	752 (67)
C(9)	1186 (10)	−1219 (19)	1491 (10)	833 (89)
C(10)	336 (9)	−2375 (22)	1263 (12)	986 (102)
C(11)	−90 (7)	−481 (24)	1044 (9)	800 (75)

[a] Equivalent Isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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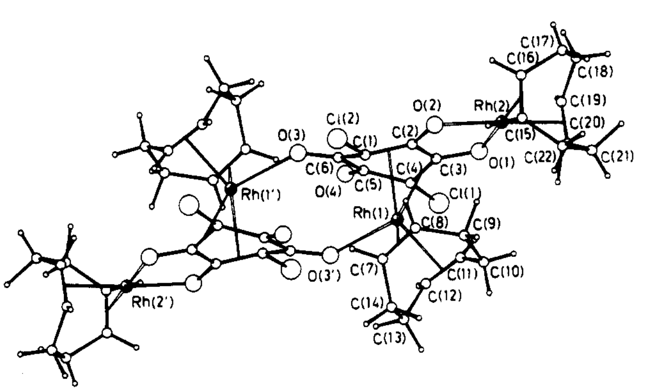

Figure 2. View of the structure of the tetranuclear complex $[Rh_4(\mu\text{-}CA)_2(cod)_4]$ (**1**) with the atomic numbering scheme.

Powernode 6040 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

Results and Discussion

Two general and well-known pathways for the synthesis of binuclear complexes of rhodium(I) are the treatment of [Rh(acac)(diolefin)] monomers or $[Rh_2(\mu\text{-}OMe)_2(diolefin)_2]$ dimers with ligands with acidic proton/s such as 1*H*-pyrrolo[2,3-*b*]pyridine,[26] 2-hydroxypyridine,[27] 1,8-diaminonaphthalene,[28] or 1,2,4-triazole.[29] By using this synthetic approach with chloranilic acid and 2,5-dihydroxy-1,4-benzoquinone, a variety of binuclear rhodium(I) complexes of general formula $[Rh_2(\mu\text{-}L)(diolefin)_2]$ as well as an unusual tetranuclear compound can be obtained.

The Unexpected Formation of a Tetranuclear Complex. When the synthesis of the binuclear complex $[Rh_2(\mu\text{-}CA)(cod)_2]$ was attempted by treatment of [Rh(acac)(cod)] with H_2CA (2:1 molar ratio) in diethyl ether at room temperature, a red crystalline compound (**1**) was formed. The elemental analysis produced the stoichiometry $[Rh_2(\mu\text{-}CA)(cod)_2]_x$, and its IR spectrum (KBr) exhibits bands at 500 (m) cm^{-1} (ν_{Rh-O}), 862 (m) cm^{-1} (ν_{C-Cl}) and, interestingly, two strong ν_{CO} absorptions at 1692 and 1620 cm^{-1}. The carbonyl stretching frequencies above 1600 cm^{-1} are associated with localized C=O groups[8] and suggest the presence of an *o*-quinone resonance form (B, Figure 1) in the solid state. The complete characterization as the unexpected tetranuclear complex of formula $[Rh_4(\mu\text{-}CA)_2(cod)_4]$ was achieved by an X-ray diffraction study (vide infra). In this compound the *o*-quinone CA^{2-} dianion displays an unusual coordination mode being bound to the three rhodium atoms via three oxygens and 1,3-diene-π-electronic system.

Complex **1** is poorly soluble in most organic solvents, but it dissolves slowly in dichloromethane or chloroform to give reddish brown solutions. However, crystallization of these solutions leads to the formation of only very small dark-brown needles of the binuclear *p*-quinone complex **2** $[Rh_2(\mu\text{-}CA)(cod)_2]$ (see below).

In order to observe the rearrangement process in solution ^1H NMR measurements were made just after the dissolution; however, the structure is not retained in solution and **2** is the only product present. Therefore, it seems that the irreversible transformation of complex **1** into **2** is very fast (Scheme I).

Scheme I

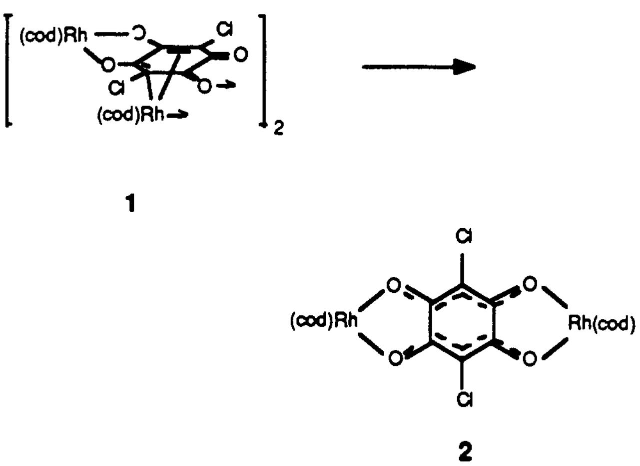

Table IV. Important Interatomic Distances (Å) and Angles (deg) in Complex **1**[a]

Rh(1)–C(1)	2.199 (6)	Rh(2)–M(5)	1.983 (9)
Rh(1)–C(2)	2.323 (7)	Rh(2)–M(6)	1.989 (8)
Rh(1)–C(3)	2.320 (7)	Cl(1)–C(4)	1.739 (6)
Rh(1)–C(4)	2.171 (6)	Cl(2)–C(1)	1.746 (6)
Rh(1)–C(7)	2.239 (8)	O(1)–C(3)	1.280 (8)
Rh(1)–C(8)	2.236 (8)	O(2)–C(2)	1.276 (9)
Rh(1)–C(11)	2.221 (7)	O(3)–C(6)	1.218 (8)
Rh(1)–C(12)	2.190 (6)	O(4)–C(5)	1.215 (9)
Rh(1)–M(1)	2.143 (6)	C(1)–C(2)	1.445 (10)
Rh(1)–M(2)	2.129 (7)	C(2)–C(3)	1.468 (8)
Rh(1)–M(3)	2.129 (7)	C(3)–C(4)	1.440 (10)
Rh(1)–M(4)	2.099 (6)	C(4)–C(5)	1.475 (9)
Rh(1)–O(3′)	2.525 (6)	C(5)–C(6)	1.523 (8)
Rh(2)–O(1)	2.079 (5)	C(1)–C(6)	1.464 (9)
Rh(2)–O(2)	2.105 (5)	C(7)–C(8)	1.380 (16)
Rh(2)–C(15)	2.094 (8)	C(11)–C(12)	1.358 (13)
Rh(2)–C(16)	2.106 (9)	C(15)–C(16)	1.386 (11)
Rh(2)–C(19)	2.103 (8)	C(19)–C(20)	1.398 (11)
Rh(2)–C(20)	2.113 (6)		
M(1)–Rh(1)–M(2)	59.1 (2)	C(2)–C(3)–C(4)	116.6 (6)
M(1)–Rh(1)–M(3)	99.5 (3)	Cl(1)–C(4)–C(3)	116.8 (5)
M(1)–Rh(1)–M(4)	145.5 (3)	Cl(1)–C(4)–C(5)	115.8 (5)
M(2)–Rh(1)–M(3)	144.7 (3)	C(3)–C(4)–C(5)	119.4 (6)
M(2)–Rh(1)–M(4)	98.0 (3)	O(4)–C(5)–C(4)	123.8 (6)
M(3)–Rh(1)–M(4)	85.3 (3)	O(4)–C(5)–C(6)	121.4 (7)
O(3′)–Rh(1)–M(1)	112.9 (2)	C(4)–C(5)–C(6)	114.5 (6)
O(3′)–Rh(1)–M(2)	107.9 (2)	O(3)–C(6)–C(1)	124.3 (6)
O(3′)–Rh(1)–M(3)	106.3 (3)	O(3)–C(6)–C(5)	121.0 (6)
O(3′)–Rh(1)–M(4)	98.0 (2)	C(1)–C(6)–C(5)	114.5 (6)
M(5)–Rh(2)–M(6)	88.8 (4)	C(8)–C(7)–C(14)	123.4 (9)
O(1)–Rh(2)–M(5)	176.2 (3)	C(7)–C(8)–C(9)	127.6 (8)
O(1)–Rh(2)–M(6)	93.9 (3)	C(8)–C(9)–C(10)	116.1 (8)
O(2)–Rh(2)–M(5)	96.0 (3)	C(9)–C(10)–C(11)	114.7 (8)
O(2)–Rh(2)–M(6)	175.0 (3)	C(10)–C(11)–C(12)	124.0 (8)
O(1)–Rh(2)–O(2)	81.2 (2)	C(11)–C(12)–C(13)	126.5 (8)
Rh(2)–O(1)–C(3)	110.3 (4)	C(12)–C(13)–C(14)	115.3 (8)
Rh(2)–O(2)–C(2)	109.6 (4)	C(7)–C(14)–C(13)	115.9 (8)
Rh(1′)–O(3)–C(6)	139.0 (4)	C(16)–C(15)–C(22)	125.9 (8)
Cl(2)–C(1)–C(2)	115.9 (5)	C(15)–C(16)–C(17)	123.5 (8)
Cl(2)–C(1)–C(6)	115.6 (5)	C(16)–C(17)–C(18)	114.2 (9)
C(2)–C(1)–C(6)	121.9 (6)	C(17)–C(18)–C(19)	113.8 (9)
O(2)–C(2)–C(1)	124.6 (6)	C(18)–C(19)–C(20)	126.2 (8)
O(2)–C(2)–C(3)	119.5 (6)	C(19)–C(20)–C(21)	123.4 (7)
C(1)–C(2)–C(3)	115.9 (6)	C(20)–C(21)–C(22)	113.6 (8)
O(1)–C(3)–C(2)	119.3 (6)	C(15)–C(22)–C(21)	114.5 (8)
O(1)–C(3)–C(4)	124.0 (6)		

[a] M(1), M(2), M(3), M(4), M(5), and M(6) are the midpoints of the C(1)–C(2), C(3)–C(4), C(7)–C(8), C(11)–C(12), C(15)–C(16), and C(19)–C(20) bonds. The primed atoms are related to the unprimed ones by the transformation $-x$, $-y$, $-z$.

Crystal Structure of $[Rh_4(\mu\text{-}CA)_2(cod)_4]$ (1). The structure of the tetranuclear complex, having crystallographically imposed C_i symmetry, is represented in Figure 2 together with the atomic numbering scheme; the most important bond distances and angles are given in Table IV. The CA^{2-} ligand, in the *o*-quinone form (B, Figure 1), is involved in a very complicate novel bonding system with three Rh atoms: it chelates to one Rh atom, Rh(2), through the O(1) and O(2) atoms, forming a pentaatomic ring [Rh(2)–O(1) = 2.079 (5) and Rh(2)–O(2) = 2.105 (5) Å], is

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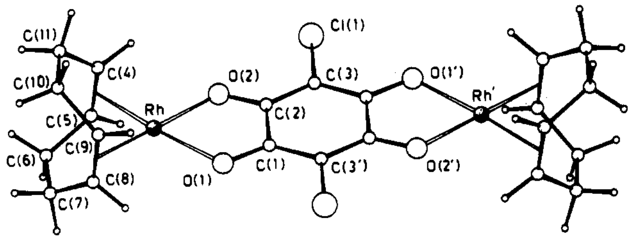
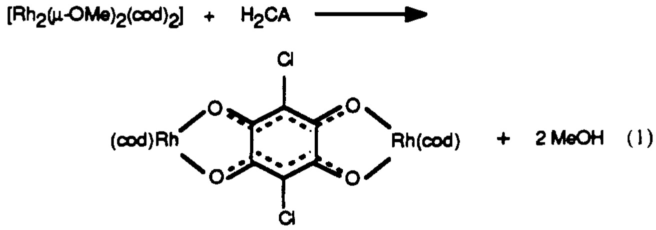


Figure 3. View of the structure of the binuclear complex [Rh$_2$(μ-CA)(cod)$_2$] (**2**) with the atomic numbering scheme.

bound to another Rh atom, Rh(1′), through the O(3) atom, even if with a rather long distance [Rh(1′)-O(3) = 2.525(6) Å], and interacts in a η^4 fashion with a third Rh atom, Rh(1), through the two adjacent C(1)–C(2) and C(3)–C(4) double bonds [Rh(1)–M(1) = 2.143 (6) and Rh(1)–M(2) = 2.129 (7) Å; M(1) and M(2) being the midpoints of the two double bonds]. Each Rh atom completes its coordination with a cod ligand interacting in the usual manner through the two double bonds. Note the different coordination geometry around the Rh atoms. If the midpoints M(5) and M(6) of the two double bonds of the cod ligand are taken into account together with the O(1) and O(2) atoms of the chelating CA^{2-} ligand, the Rh(1) atom displays a square planar coordination. The pentaatomic chelation ring shows the O(2)C(2)C(3)O(1) moiety strictly planar with the Rh atom out of 0.083 (1) Å from the mean plane through it. The coordination around Rh(1) can be described as square pyramidal with the midpoints M(3) and M(4) of the two double bonds of the cod ligand and the midpoints M(1) and M(2) of the double bonds of the CA^{2-} ligand occupying the basal plane and the O(3) atom from another CA^{2-} ligand occupying the apical site [the Rh(1) is displaced by 0.0585 (2) Å from the mean basal plane toward the apical O(3) atom].

The structural features of the CA^{2-} ligand are in agreement with the *o*-quinone form: the values of the distances of the two formal C(1)–C(2) and C(3)–C(4) double bonds, 1.445 (10) and 1.440 (10) Å, have undergone the expected elongation because of the two π interactions with the metals: that of the C(5)–C(6) distance, 1.523 (8) Å, is in accord with a single bond character; those of the two C(2)–O(2) and C(3)–O(1) bonds, 1.276 (9) and 1.280 (8) Å, are longer than the two C(5)–O(4) and C(6)–O(3) bonds, 1.215 (9) and 1.218 (8) Å, these latter in accord with the normal benzoquinone ones for double bond localization in the carbonyl group. A novel feature of this ligand, involved in a very complicate bonding with three metals, is the loss of the planarity, the six-membered ring showing a "boat" conformation with the two planar C(1)C(2)C(3)C(4) and C(1)C(6)C(5)C(4) moieties tilted by 31.6 (3)°. The Cl(1), Cl(2), O(1), and O(2) atoms deviate by 0.088 (2), 0.051 (2), 0.036 (5), and 0.077 (5) Å, on the same side, from the mean plane through the C(1)C(2)C(3)C(4) moiety, whereas the Cl(1), Cl(2), O(3) and O(4) atoms deviate by 0.108 (2), 0.014 (2), 0.199 (5), and 0.007 (6) Å, on the same side, from the mean plane through the C(1)C(6)C(5)C(4) moiety, the most remarkable deviation corresponding to the O(3) atom involved in an interaction with the Rh(1) atom.

Binuclear Complexes. The binuclear compound [Rh$_2$(μ-CA)(cod)$_2$] (**2**) can be straightforwardly obtained as dark-brown needles, suitable for X-ray diffraction studies, and in 90% yield, by slow crystallization of a diethyl ether solution of [Rh$_2$(μ-OMe)$_2$(diolefin)$_2$] and H$_2$CA according to eq 1. In this complex, the CA^{2-} dianion, in the *p*-quinone form, chelates to the two rhodium(I) atoms through the four oxygen atoms and acts as a tetradentate ligand.



(1)

Table V. Important Interatomic Distances (Å) and Angles (deg) in Complex **2**[a]

Rh–O(1)	2.100 (9)	C(1)–C(2)	1.520 (14)
Rh–O(2)	2.089 (8)	C(2)–C(3)	1.381 (15)
Rh–C(4)	2.080 (12)	C(3)–C(1′)	1.396 (17)
Rh–C(5)	2.088 (15)	C(4)–C(5)	1.39 (2)
Rh–C(8)	2.141 (15)	C(4)–C(11)	1.50 (2)
Rh–C(9)	2.113 (15)	C(5)–C(6)	1.47 (2)
Rh–M(1)	1.965 (14)	C(6)–C(7)	1.52 (3)
Rh–M(2)	2.005 (15)	C(7)–C(8)	1.38 (3)
Cl(1)–C(3)	1.724 (10)	C(8)–C(9)	1.42 (2)
O(1)–C(1)	1.283 (15)	C(9)–C(10)	1.50 (3)
O(2)–C(2)	1.257 (15)	C(10)–C(11)	1.45 (2)
M(1)–Rh–M(2)	87.4 (6)	C(1)–C(2)–C(3)	118.9 (9)
O(1)–Rh–M(2)	98.1 (5)	Cl(1)–C(3)–C(2)	119.4 (8)
O(2)–Rh–M(1)	95.5 (4)	C(2)–C(3)–C(1′)	121.0 (10)
O(1)–Rh–O(2)	79.0 (3)	C(5)–C(4)–C(11)	123.5 (11)
Rh–O(1)–C(1)	113.0 (7)	C(4)–C(5)–C(6)	125.3 (12)
Rh–O(2)–C(2)	113.7 (6)	C(5)–C(6)–C(7)	115.2 (12)
O(1)–C(1)–C(2)	116.3 (9)	C(6)–C(7)–C(8)	114.9 (15)
O(1)–C(1)–C(3′)	123.6 (9)	C(7)–C(8)–C(9)	125.9 (17)
C(2)–C(1)–C(3′)	120.0 (9)	C(8)–C(9)–C(10)	124.3 (15)
O(2)–C(2)–C(1)	117.3 (9)	C(9)–C(10)–C(11)	115.3 (14)
O(2)–C(2)–C(3)	123.8 (10)	C(4)–C(11)–C(10)	116.2 (14)

[a] M(1) and M(2) are he midpoints of the C(4)–C(5) and C(18)–C(19) bonds. The primed atoms are related to the unprimed ones by the transformation $^1/_2 - x$, $^1/_2 - y$, $-z$.

Complex **2** dissolves in dichloromethane or diethyl ether faster than **1**, and according to the spectroscopic data of freshly prepared solutions of complexes **1** or **2**, only compound **2** is present in solution. Attempts to prepare the tetranuclear compound **1** from a saturated diethyl ether solution of compound **2** were unsuccessful.

The UV–visible spectra of compound **2**, in dichloromethane, exhibit transitions at 330 and 445 nm. These bands are most likely associated with π–π^* transitions.[30] The feature at 445 nm is indicative of the presence of one quinone resonance form (B,C, Figure 1) because in complexes where the chloranilate dianion coordinates as a bis(carbanion) (A, Figure 1), as in K$_2$[Pd(*c*-CA)Cl$_2$]·0.5H$_2$O,[16a] this band is absent. The ^{1}H NMR spectra in CDCl$_3$ display a single peak at δ 4.37, suggesting the equivalence of the eight olefinic protons according to a D_{2h} symmetry associated with the *p*-quinone resonance form in the ligand (C, Figure 1). Further evidence comes from the ^{13}C{^{1}H} NMR spectra in CDCl$_3$. For the olefinic carbons only one resonance at δ 80 is present. This chemical shift, as well as the Rh–C coupling constant of 14 Hz, is in the normal range for π-bonded olefins in square-planar complexes of rhodium(I).[31] The eight equivalent methylenic carbons display a single peak at δ 31. A singlet at δ 180, in the expected range for the *p*-quinones,[30] is observed for the carbonyl carbons. The resonance corresponding to the C–Cl carbons is not observed. Thus, only the binuclear complex **2** is present in solution.

In the solid state, the IR (KBr) of **2** is in agreement with the species observed in solution. It shows two ν_{CO} stretching absorptions at 1500 (vs) and 1370 (s) cm^{-1}, in good agreement with the D_{2h} symmetry[32] expected in the ligand and also consistent with a C–O bond order of 1.5.[13]

We have also tested both synthetic routes with the diolefins norborna-2,5-diene (nbd) and tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene (tfb), as well as the related ligand 2,5-dihydroxy-1,4-benzoquinone, but in these cases, only the binuclear complexes

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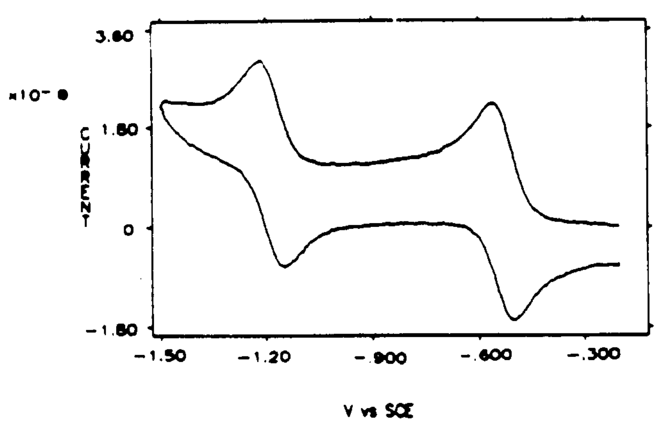


Figure 4. Cyclic voltammogram (scan rate 100 mV s^{-1}) at a platinum electrode for reduction of $[Rh_2(\mu\text{-DHBQ})(cod)_2]$ (5×10^{-4} mol/L) in CH_2Cl_2 (0.2 mol/L TBAH).

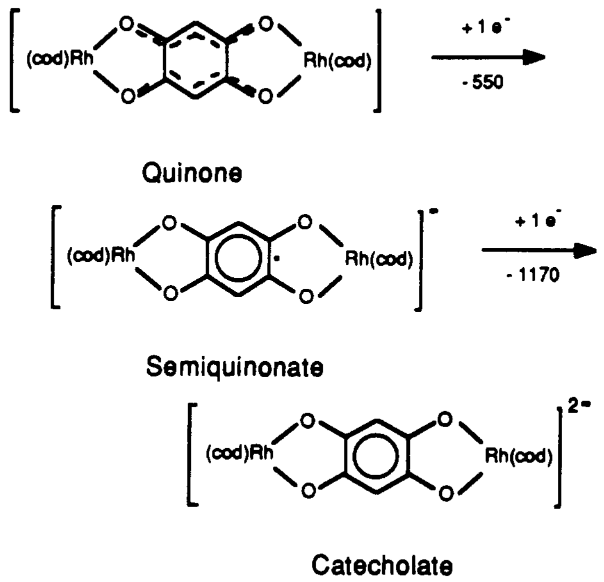
$[Rh_2(\mu\text{-L})(diolefin)_2]$ {L = CA^{2-}, diolefin = ndb (**3**), tfb (**4**); L = $DHBQ^{2-}$, diolefin = cod (**5**), nbd (**6**), tfb (**7**)} are obtained.

Complexes **3**–**7** are sparingly soluble in organic solvents, and it seems plausible that the insolubility of the thermodynamically more stable species prevents the isolation of any other compounds.

Crystal Structure of $[Rh_2(\mu\text{-CA})(cod)_2]$ (2). The structure of the binuclear complex, having a crystallographic imposed C_i symmetry, is shown in Figure 3 together with the atomic numbering scheme; the most important bond distances and angles are given in Table V. The CA^{2-} ligand, in the more common *p*-quinone form (C, Figure 1), chelates to two Rh centers through the oxygen atoms as a tetradentate ligand. The lengths of the Rh–O(1) and Rh–O(2) bonds, 2.100 (9) and 2.089 (8) Å, and of the C(1)–O(1) and C(2)–O(2) bonds, 1.283 (15) and 1.257 (15) Å, are comparable to those found in **1** for the Rh–O and C–O bonds involving the chelating O atoms. The Rh atom completes its coordination with a cod ligand interacting in the usual η^2 manner through the two double bonds. If the midpoints M(1) and M(2) of the two double bonds of the cod ligand are taken into account [Rh–M(1) = 1.965 (14) and 2.005 (15) Å] together with the O(1) and O(2) atoms of the chelating CA^{2-} ligand, the Rh atom displays a square planar coordination. In the pentaatomic chelation ring the Rh atom is 0.188 (2) Å out of the plane through the O(1)C(1)C(2)O(2) atoms.

The CA^{2-} ligand as a whole is practically planar with π-electron delocalization confined to upper and lower region of the ligand, the C(1)–C(2) bond length of 1.520 (14) Å being indicative of negligible conjugation between halves of the ligand. The structural features of the CA^{2-} ligand are comparable to those found in other chloranilate complexes such as $[Ni_2(tren)_2(CA)]^{2+}$ (tren = 2,2′,2″-triaminotriethylamine), $[Cu_2(Me_5dien)_2(CA)]^{2+}$ (Me_5-dien = 1,1,4,7,7-pentamethyldiethylenetriamine),[8] and $[(MoO_2Cl_2)_2(CA)]^{2-}$,[12a] where it behaves as a tetradentate bis-chelating ligand in a manner resembling that shown by the oxalate dianion.

Electrochemical Properties. The electrochemistry of $[Rh_2(\mu\text{-CA})(cod)_2]$ (**2**) and $[Rh_2(\mu\text{-DHBQ})(cod)_2]$ (**5**) was investigated by linear-sweep voltammetry with a RDE and cyclic voltammetry. The reduction response of the binuclear complex **5** at the RDE at 21 °C in dichloromethane over the potential range 0 to −1500 mV (vs SCE) consists of two well-defined reduction waves with similar limiting currents per concentration unit. The reversibility of these reductions was established by cyclic voltammetry since well-shaped reoxidation waves were seen in the backward scan (Figure 4). The characteristics of these waves in the scan rate range 50–1000 mV s^{-1} are as follows: $E°$, −550, −1170 mV; ΔE_p,[33] 63 (±3), 62 (±2) mV; i_{p_c}/i_{p_a}, 0.99 (±0.02), 0.98 (±0.03). $i_{p_c}v^{1/2}$ is constant. Thus, compound **5** was electrochemically reduced by two stepwise, reversible one-electron transfer showing an EE reduction mechanism.[34] These two redox processes can be reasonably attributed to the quinone-semiquinonate and to the semiquinonate-catecholate couples (eq 2) in agreement with the ligand centered transfer processes observed for other metal-$DHBQ^{2-}$ adducts.[12c]



(2)

Analogous reduction processes are observed for complex **2**. The couple semiquinonate–catecholate appears as a reversible one electron redox process; however, the couple quinone–semiquinonate is not reversible indicating that structural changes such as dimerization or loss of chloride ions are taking place on the time scale of experiment.

Concluding Remarks. In this work we have synthesized and characterized six new binuclear rhodium(I) complexes using as bridging ligands the CA^{2-} or $DHBQ^{2-}$ dianions. In these complexes the CA^{2-} or $DHBQ^{2-}$ dianions in the *p*-quinone form chelate to two rhodium(I) atoms as tetradentate ligands. The dianions are planar with delocalization confined to upper and lower regions of the ligand rings. We have also described the preparation and the structural characterization of the interesting tetranuclear complex $[Rh_4(\mu\text{-CA})_2(cod)_4]$, in which the CA^{2-} ligand, in the *o*-quinone form, presents an unexpected and novel coordination mode for a metal chloranilate compound.

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Supplementary Material Available: Hydrogen atom coordinates and isotropic thermal parameters (Table SI), anisotropic thermal parameters for the non-hydrogen atoms (Table SII), and complete bond distances and angles (Table SIII) for compound **1**, hydrogen atom coordinates and isotropic thermal parameters and anisotropic thermal parameters for the non-hydrogen atoms (Tables SIV and SV) and complete bond distances and angles (Table SVI) for compound **2**, and crystallographic data for both compounds (Table SVII) (7 pages). Ordering information is given on any current masthead page.

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(33) The separation between the anodic and cathodic peak potentials (ΔE_p) is approximately equal to the value observed under the same experimental conditions for a reversible one-electron transfer without compensation of solution resistance (ΔE_p = 62 (±3) mV, ferrocene oxidation).

(34) Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 831.