

distorted as to be unsatisfying as a seven-coordinate system. A tetracoordinate picture is probably more realistic and will be used for the molecular orbital treatment below.

The effective atomic number (EAN) for tungsten requires that only ten electrons should be donated by the acetylenic ligands. This means two of the acetylenic ligands donate both their π -electron pairs (similar to $\text{Pt}(\text{R}_3\text{P})_2\text{ac}^{23}$ and $\text{ReCl}(\text{ac})_2^{24}$) and the third only one. Since proton magnetic resonance, however, indicates that all acetylene ligands are bonded equivalently, we have to assume that the lone electron pair is resonated through the entire carbon system.

A qualitative MO scheme derived from overlap of appropriate AO's of the metal with the ligands is given in Fig. 5. The two excess electrons may occupy a lone pair a_2 ligand MO which nicely explains the diamagnetism of this complex.

If we consider structure b in Fig. 3 with a C_3 symmetry, the simple Hückel MO treatment does not change the qualitative picture. The ligand π -orbital system may be overlapped in the same way with the metal AO's as shown. In this case also, the excess pair of electrons enters a nonbonding a-orbital. Since the acetylene ligands are twisted to the C_3 axis and the π -orbitals of the $\text{C}\equiv\text{C}$ bond also have to be twisted to each other to give a reasonable overlap with the metal

AO's, a more accurate treatment becomes rather cumbersome.

Conclusions

Tris(hexyne)tungsten(0) monocarbonyl, tris(diphenylacetylene)tungsten(0) monocarbonyl, and tris(methylphenylacetylene)tungsten(0) monocarbonyl constitute a unique new group of complexes of tungsten. The structures of all three are similar, with the ligands arranged symmetrically around the metal and doubly π -complexed through the $\text{C}\equiv\text{C}$. The presence of only one CO is confirmed by chemical and spectroscopic evidence. Similar complexes are not obtained with Cr or Mo or with terminal alkynes. Although the electronic picture for these complexes is most unusual, in that there are two more electrons than necessary for tungsten's EAN, a simple MO treatment shows that the electron pair can be accommodated in a suitable nonbonding orbital in either a C_{3v} or C_3 symmetry. Further confirmation of structure must await an X-ray crystallographic analysis which is currently underway.³⁹

Acknowledgment.—We are indebted to Prof. Herbert Kaesz (Department of Chemistry, U.C.L.A.) for his helpful discussions and to Mr. Herbert Grossman for his experimental assistance.

(39) L. F. Dahl, University of Wisconsin, Madison, Wis.

[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY, UNIVERSITY OF MUNICH, GERMANY]

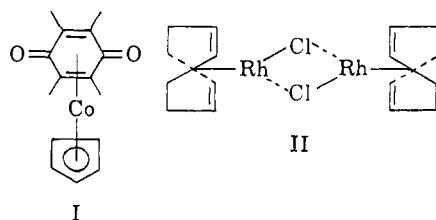
Preparation and Properties of Some Duroquinone π -Complexes of Cobalt, Rhodium, and Iridium^{1,2}

BY G. N. SCHRAUZER AND K. C. DEWHIRST³

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The reduction of rhodium and iridium trichlorides with ethanol in the presence of duroquinone yields duroquinone π -complexes of rhodium(I) and iridium(I) chlorides, respectively. Reaction with cyclopentadienylsodium produces the very stable duroquinonecyclopentadienylmetal compounds, which are compared with the previously prepared cobalt complex. The electronic spectra of these complexes are discussed, and the observed transitions are calculated on a semiempirical basis, using simple MO theory. From the infrared spectra of the complexes, it is concluded that the π -bonded duroquinone molecule must be nonplanar, and an explanation for this effect is given.

Recently, the electronic spectra of a number of quinone π -complexes of nickel were successfully interpreted on the basis of a molecular orbital treatment.⁴ This



work is now being extended to complexes of other transition metals. It was reported a short time ago² that dicarbonylcyclopentadienylcobalt reacts with duroqui-

none to produce a duroquinone complex of cobalt, $\text{DquCoC}_5\text{H}_5$ (I). In view of its remarkable stability and its well-resolved electronic spectrum, it appeared to be of interest to prepare the analogous complexes of rhodium and iridium.

Results

Duroquinone π -Complexes of Rhodium.—The Rh(I) valence state may be stabilized with chelating dienes. If rhodium trichloride is reduced with hot ethanol in the presence of, *e.g.*, 1,5-cyclooctadiene, the dimeric cyclooctadienechlororhodium(I), compound II, is obtained.^{5,6} We have made use of this reaction to prepare duroquinone π -complexes of rhodium(I) chloride. Refluxing solutions of duroquinone and $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ in ethanol for 3 hr. yields, in addition to small amounts of a soluble complex, an insoluble orange product which roughly analyzes for $(\text{DquRhCl})_x$. This complex (III) is probably a halogen-bridged coordination polymer. It reacts with pyridine to produce a red bispyridine adduct (IV)

(1) Paper VIII on Quinone π -Complexes of Transition Metals; presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

(2) Paper VII: G. N. Schrauzer and H. Thyret, *Angew. Chem.*, **75**, 641 (1963).

(3) Visiting Fellow, 1962–1963, Shell Development Company, Emeryville, Calif.

(4) G. N. Schrauzer and H. Thyret, *Theoret. Chim. Acta*, **1**, 172 (1963).

(5) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(6) G. Wilkinson, M. A. Bennett, and E. W. Abel, *ibid.*, 3178 (1959).

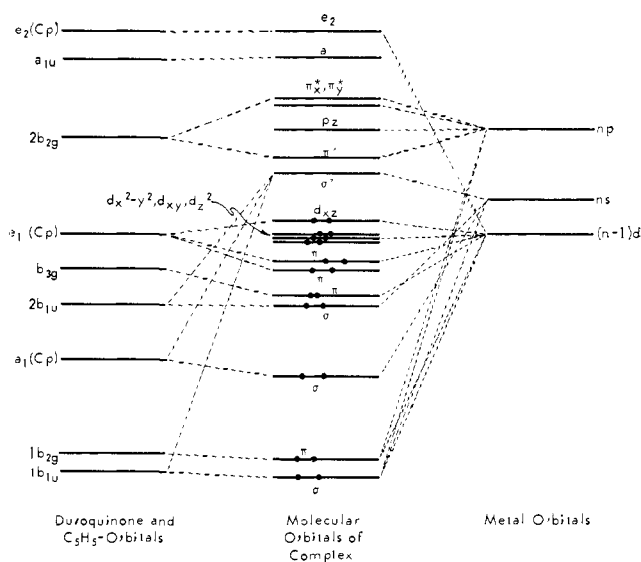
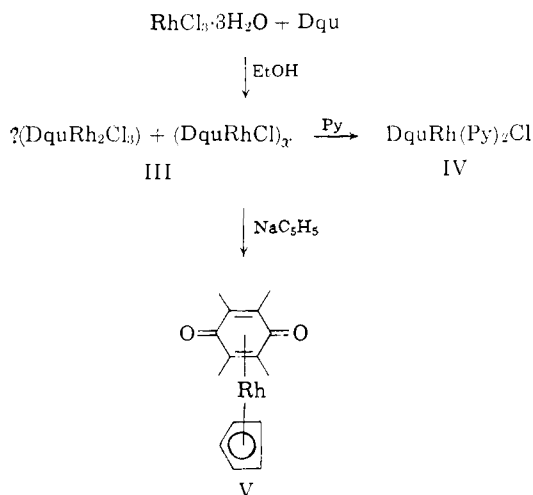


Fig. 1.—Schematic energy level diagram for complexes of the type $DquMC_5H_5$: the coulomb terms of the Dqu, C_5H_5 , and metal orbitals are only approximate and the adopted sequence is not necessarily correct.

which is monomeric in chloroform. The soluble complex, of which only small amounts were isolated, is not well characterized. It analyzes roughly for $DquRh_2Cl_3$ and is soluble only in water and alcohol. Both complexes must contain π -bonded duroquinone, however, as they react with cyclopentadienylsodium to produce duroquinonecyclopentadienylrhodium (V), a yellow-orange, crystalline, air-stable, water-soluble, sublimable complex, which is stable up to 295° .

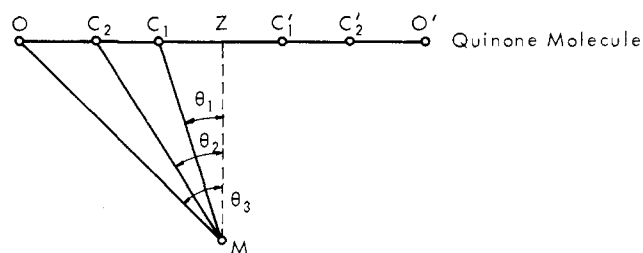
The infrared spectrum of V shows a doublet in the carbonyl region at 1580 and 1532 cm.^{-1} (KBr). The large decrease of the $C=O$ stretching frequencies compared with duroquinone (1629 cm.^{-1}) indicates strong electron back-donation, and the splitting suggests that the π -bonded duroquinone molecule may not be planar. The n.m.r. spectrum of V consists of two resonances at τ 4.85 and 7.85, with an intensity ratio of 5:12. Expansion of the spectrum reveals that the resonance at τ 4.85 is actually a doublet ($J = 1.1\text{ c.p.s.}$) due to coupling of



the cyclopentadienyl proton spins with ^{103}Rh ($I = 1/2$).⁷

Duroquinone π -Complexes of Iridium—When iridium trichloride is treated with duroquinone as above,

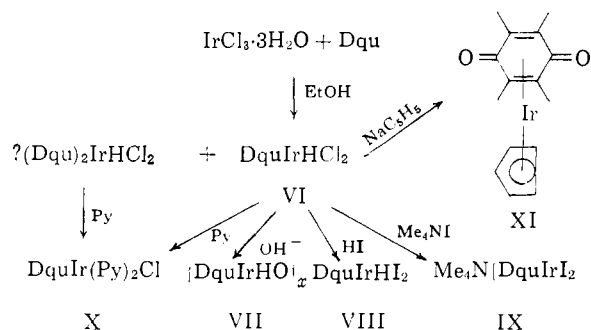
(7) For similar observations see K. S. Brenner, E. O. Fischer, H. P. Fritz, and C. G. Kreiter, *Chem. Ber.*, **96**, 2632 (1963).



	Co	Rh	Ir	(A)
$M - C_1 = M - C'_1$	2.0	2.1	2.2	
$M - C_2 = M - C'_2$	2.0	2.1	2.2	
$M - C_3 = M - C'_3$	3.0	3.1	3.25	
θ_1	$44^\circ 38'$	$42^\circ 5'$	$39^\circ 45'$	
θ_2	$44^\circ 38'$	$42^\circ 5'$	$39^\circ 45'$	
θ_3	$63^\circ 13'$	$59^\circ 50'$	$56^\circ 40'$	

Fig. 2.—Model for the calculation of the metal-quinone overlap integrals.

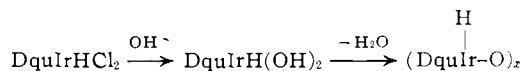
the main product is a water-soluble complex of approximate composition $DquIrHCl_2$ (VI). Although this



material could not be obtained completely pure, its composition was verified by reaction with hydrogen iodide to give the corresponding iodide VIII, and by reaction with tetramethylammonium iodide to give the salt IX.

A small quantity of insoluble complex was obtained in addition to VI by filtration of the reaction mixture and has the approximate composition $(Dqu)_2IrHCl_2$. When heated with water this compound readily splits off duroquinone, and when treated with pyridine it gives X, the same material obtained by treatment of VI with pyridine. Compound X is thermochromic, a nonelectrolyte in nitrobenzene, and does not react with sodium tetraphenylboron. The n.m.r. spectrum shows in addition to the pyridine resonances a single, sharp signal at τ 8.85 due to the duroquinone protons.

Treatment of VI with sodium hydroxide gives an insoluble, crystalline complex VII, which analyzes for $(DquIrHO)_x$. The infrared spectrum of this material (KBr) is very similar to that of VI, except for the presence of a medium band at 2225 cm.^{-1} , indicative of a metal-hydrogen bond. This material is probably a polymeric duroquinonehydrido-iridium oxide, being formed as



Finally, treatment of VI with cyclopentadienylsodium affords cream-colored duroquinonecyclopentadienyliridium (XI), m.p. 315° dec. The infrared

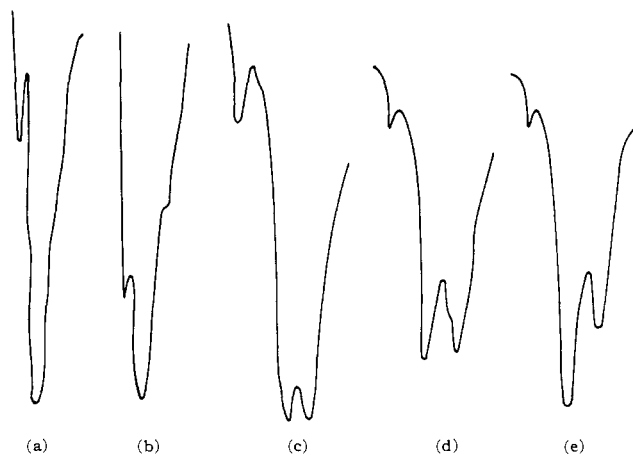


Fig. 3.—Duroquinone carbonyl absorptions in metallic complexes: Bisduroquinonenickel (a), $C_8H_{10}NiDqu$ (b), $DquCoC_8H_5$ (c), $DquRhC_8H_5$ (d), and $DquIrC_8H_5$ (e), all measured in KBr. Similar splittings were observed in chloroform.

spectrum of XI exhibits carbonyl absorptions at 1590 and 1545 cm^{-1} (KBr); the n.m.r. signals of the cyclopentadienyl and duroquinone protons were found at τ 4.67 and 7.87, in the ratio 5:12, respectively.

Discussion

Electronic Structure.—The discussion of electronic structure will be restricted to complexes of the type $DquMC_8H_5$, for which a schematic orbital diagram is given in Fig. 1. This diagram requires little comment; the available 22 electrons can be placed into ten bonding or practically nonbonding orbitals. The highest occupied orbital is mainly localized on the metal atoms of the d_{xz} -type; a model calculation for the cobalt complex, in which overlap integrals calculated for the Co-quinone and those for the Co- C_8H_5 interactions were used (*vide infra*), indicates that it is only slightly antibonding. One therefore may expect greater stability and somewhat smaller metal to ligand distances in the cobalt complex than in the compounds of the type diene-Ni-Dqu, or bis(duroquinone)nickel, in which the highest occupied orbital has considerable antibonding character.⁴ To compare the stabilities of the iso-electronic duroquinone complexes of Co, Rh, and Ir, the group-overlap integrals of the metal-ligand interactions were calculated by standard methods, using models with the assumed geometry in Fig. 2. The assumed bond distances and angles are of course only approximate but this will be sufficient for our purposes. Most of the constituent atomic-overlap integrals were taken from published tables.^{8,9} The parameters p and t were calculated for the configuration $(n-1)d^7ns^2$ and Slater's rules were applied for determining the α -values. For the integrals which involve quantum number 6, extrapolated values were used. For the calculation of the group-overlap integrals, the eigenvectors for the quinone MO's were taken from ref. 4 in order to obtain values comparable with those calculated for the nickel com-

(8) R. S. Mulliken, *et al.*, *J. Chem. Phys.*, **17**, 1248 (1949); H. H. Jaffé, *ibid.*, **21**, 258 (1953); H. H. Jaffé and G. O. Doak, *ibid.*, **21**, 196 (1953); L. Leifer, F. A. Cotton, and J. R. Leto, *ibid.*, **28**, 364 (1958); D. A. Brown, *ibid.*, **29**, 1086 (1958).

(9) Although $S(2p\pi 4d\pi)$ may be calculated according to D. A. Brown [*J. Chem. Soc.*, 690 (1961)], we have used interpolated values between $S(2p\pi 3d\pi)$ and $S(2p\pi 5d\pi)$, mainly because the $A_n(p)$ functions have not been tabulated up to $p = 10.00$. For this reason the calculation could not be completed and the use of interpolated values appeared to be more favorable.

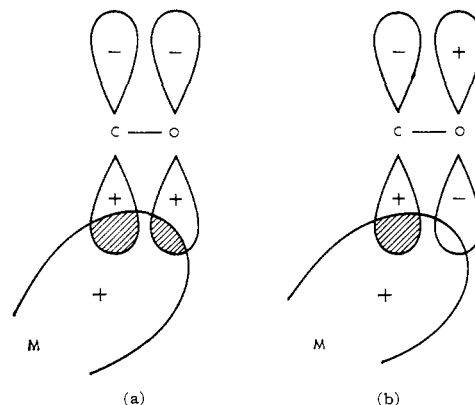


Fig. 4.—Bonding (a) and repulsive (b) conditions for the metal-oxygen interaction in a quinone π -complex.

plexes. The obtained values are listed in Table I. As may be seen, the overlap integrals involving d-orbitals all increase in the order $Co < Rh < Ir$, indicating that π - and δ -bonding become more important in the heavier metals. σ -Bonding interactions involving the d_{z^2} and p_z orbitals also increase in this order, but the overlap integrals $S(ib_{1u}-ns)$ are smaller for $n = 6$ than those for $n = 4$ and 5. One might thus expect the complex stabilities to vary in the order $Co < Rh \leq Ir$. Calculations for $M-C_8H_5$ interactions suggest a similar trend.

TABLE I
CALCULATED OVERLAP INTEGRALS FOR THE METAL-QUINONE INTERACTIONS IN THE COMPLEXES $DquMC_8H_5^a$

	Co ($n = 4$)	Rh ($n = 5$)	Ir ($n = 6$)
$S(ib_{1u}-ns)$			
$i = 1$	0.213	0.256	(0.152)
2	.154	.259	(.075)
3	.008	.043	(.013)
$S(ib_{1u}-np_z)$			
$i = 1$.015	.031	(.068)
2	.032	.026	(.041)
3	.017	.007	(.004)
$S(ib_{2g}-np_x)$			
$i = 1$.287	.332	(.273)
2	.168	.209	(.106)
3	.002	.003	(.007)
$S(b_{2g}-(n-1)d_{yz})$.132	.239	.328
$S(ib_{2g}-(n-1)d_{zz})$			
$i = 1$.080	.166	.235
2	.100	.178	.238
3	.014	.017	.083
$S(b_{3g}-np_y)$.301	.356	(.277)
$S(ib_{1u}-(n-1)d_{x^2-y^2})$			
$i = 1$.159	.209	.241
2	.039	.112	.136
3	.015	.056	.063
$S(a_{1u}-(n-1)d_{xy})$.136	.208	.239
$S(ib_{1u}-(n-1)d_{z^2})$			
$i = 1$.054	.070	.102
2	.031	.028	.044
3	.019	.018	.027

^a Extrapolated values are placed in parentheses.

It was mentioned earlier that the π -bonded duroquinone molecule should be nonplanar to account for the doublet carbonyl band in the infrared spectrum. In Fig. 3, the C=O bonds of a number of duroquinone complexes are shown. In Fig. 4, it may be seen that the interaction of a metal orbital with the π -orbitals of the carbonyl would give rise to a repulsive, and thus nonplanar, condition, if a node passes between the car-

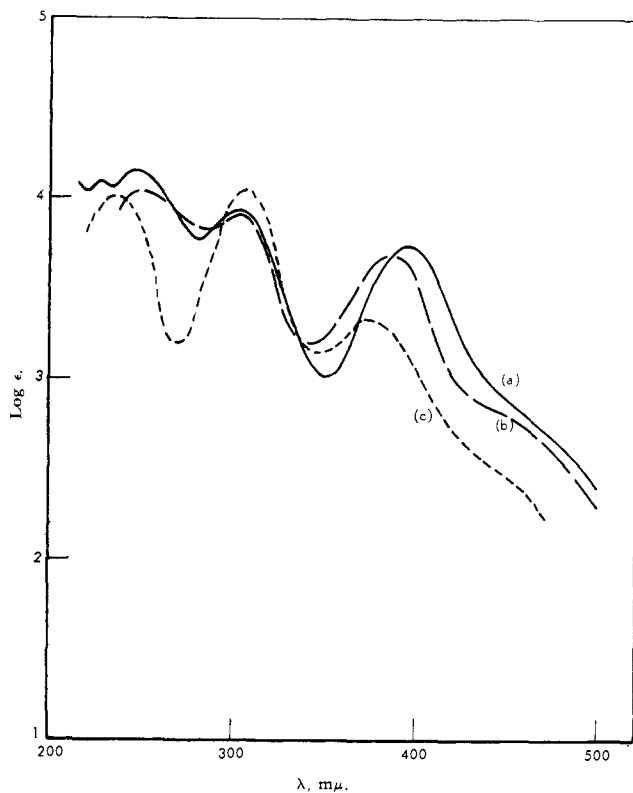


Fig. 5.—Absorption spectra of $DquCoC_5H_5$ in H_2O (a), $CHCl_3$ (b), and $HClO_4$ (c).

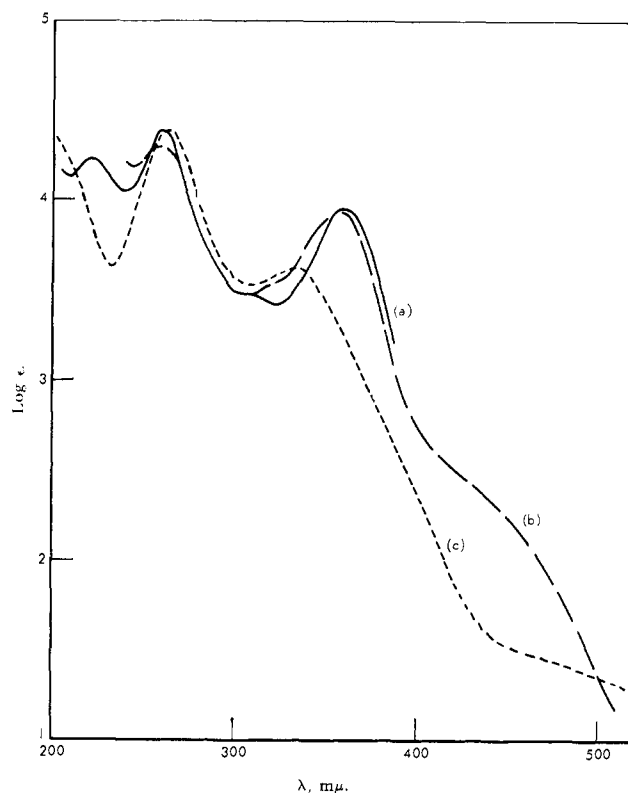


Fig. 7.—Absorption spectra of $DquRhC_5H_5$ in H_2O (a), $CHCl_3$ (b), and $HClO_4$ (c).

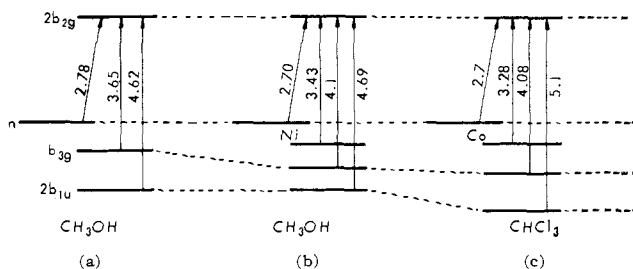


Fig. 6.—Experimental term-level schemes for duroquinone (a), C_5H_5NiDqu (b), and $DquCoC_5H_5$ (c).

bon and oxygen atoms. For the important interactions involving the $2b_{1u}$ and $2b_{2g}$ quinone orbitals, this is the case. Such a distortion has been reported¹⁰ in tetramethylcyclopentadienonecyclopentadienylcobalt.

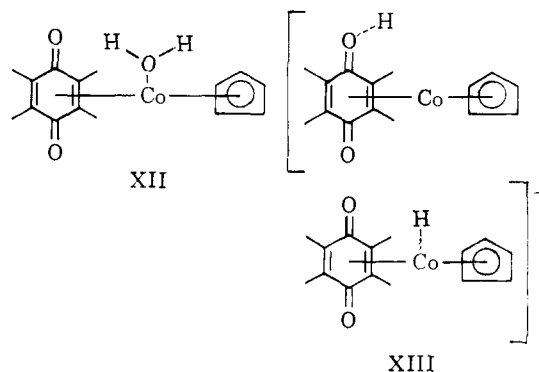
Electronic Spectra.—The absorption spectra of duroquinonecyclopentadienylcobalt (I) in various media are given in Fig. 5, the assignments for which have already been reported.² The term-level schemes of I, cyclooctatetraeneduroquinonenickel, and duroquinone are shown in Fig. 6. As is to be expected from the similarity of overlap integrals, the term-level schemes are very similar, with a somewhat greater orbital stabilization in the case of cobalt.

As may be seen from Fig. 5, the intense charge-transfer band at $388\text{ m}\mu$ ($\epsilon\ 5000$) undergoes a bathochromic shift of $7\text{ m}\mu$ in passing from chloroform to water, whereas the remaining bands are unaffected. This shift may be due to a weak solvation of the cobalt atom as in XII.

In perchloric acid solution, however, all of the bands except the $b_{3g}-2b_{2g}$ transition at $305\text{ m}\mu$ (8300) undergo a hypsochromic shift. This effect is best explained by

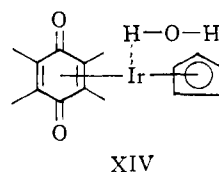
(10) L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **83**, 752 (1961).

assuming a protonation of both the metal atom and the quinone oxygens as in XIII. It is interesting to note



that the band at $226\text{ m}\mu$ ($13,000$) evidently undergoes a hypsochromic shift which suggests that it could be the $3d-\pi^*_{Cp}$ charge-transfer band.

The spectra of the corresponding rhodium and iridium complexes V and XI in various solvents are presented in Fig. 7 and 8. As may be seen, the spectra are similar to that of cobalt, except that in the case of rhodium a new band appears at $314\text{ m}\mu$ (3000) which is also present in cyclooctadiene-(1,5)-cyclopentadienylrhodium and bisethylenecyclopentadienylrhodium.¹¹ This



XIV

(11) We are indebted to Dr. R. Cramer, E. I. du Pont de Nemours and Co., Central Research Department, Wilmington, Del., for making a spectrum of this complex available to us.

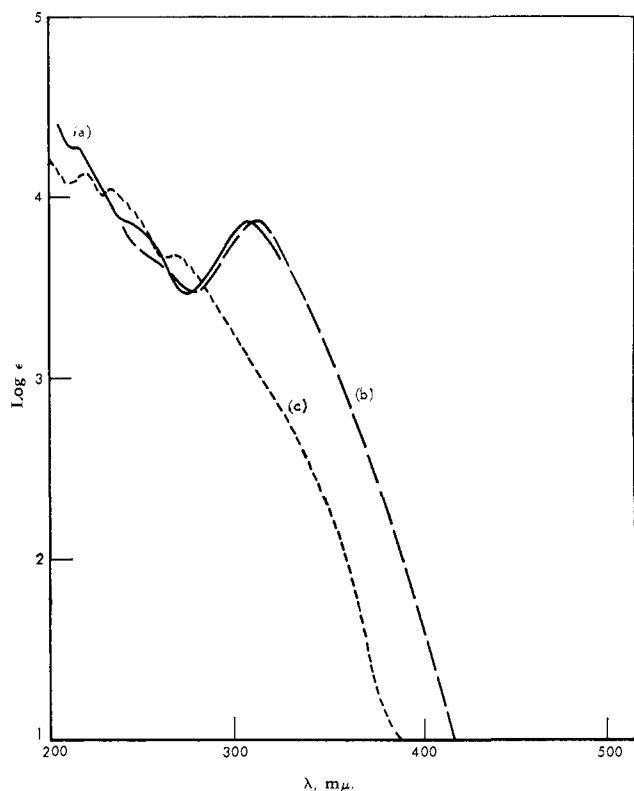


Fig. 8.—Absorption spectra of $DquIrC_5H_5$ in H_2O (a), $CHCl_3$ (b), and $HClO_4$ (c).

band could be a $4d-5p^*$ transition. Solvatochromic effects of the charge-transfer bands in passing from chloroform to water were also observed here, but the magnitude of the bathochromic shift is smaller for rhodium and becomes hypsochromic for iridium. It may be possible that in the latter case water is actually protonating the iridium atom as in XIV.

In perchloric acid solution, the rhodium compound exhibits nearly the same spectral shifts as cobalt. The iridium compound, although it shows the typical hypsochromic shift of the charge-transfer band, exhibits a somewhat different pattern for the remaining two bands. To explain the nature of these shifts, a more detailed theoretical treatment would be necessary.

The experimental term-level schemes resulting from the assignments of the observed bands for the entire series are shown in Fig. 9. The diagrams were drawn on the assumption that the nonbonding electron pairs on duroquinone have equal energies throughout the series. The stability order $Co < Rh \leq Ir$ may be clearly seen.

In order to correlate the observed band shifts with the calculated overlap integrals, a simple model calculation was performed. Considering only the metal-quinone interactions and neglecting the effect of metal p orbitals, the secular determinants were solved for the quinone interactions with Co, Rh, and Ir with matrix elements chosen as follows. The diagonal elements were based upon a value of 8.0 e.v. for the energy of the $(n-1)d_{ns}$ orbitals of cobalt and rhodium, and of 8.5 e.v. for iridium; these values are not very different from the first ionization potentials of these metals. The energy of the duroquinone b_{3g} orbital was placed at 9.0 e.v. and the energy separations of this orbital with the $2b_{1u}$ and $2b_{2g}$ orbitals were taken from the electronic

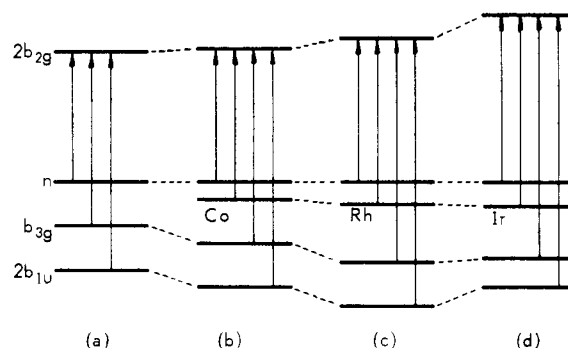


Fig. 9.—Experimental term-level schemes for duroquinone (a), $DquCoC_5H_5$ (b), $DquRhC_5H_5$ (c), and $DquIrC_5H_5$ (d).

spectrum of duroquinone. The energies of the remaining Dqu orbitals were approximated from the calculated orbital energies,⁴ with $\beta = 3.00$ e.v. The off-diagonal elements were approximated by assuming a proportionality to the magnitudes of overlap. Putting an overlap value of 0.200 equal to 1 e.v. of bond energy, the various orbital energies may be calculated, from which one obtains the transition energies listed in Table II, together with the experimental values. The agreement between the calculated and observed transition energies is better than expected and may be fortuitous in view of various approximations employed. Nonetheless, this result leaves no doubt that the assignments of the observed bands in the spectra of these compounds are correct.

TABLE II
CALCULATED AND OBSERVED TRANSITION ENERGIES IN
COMPLEXES OF THE TYPE $DquMC_5H_5$

Transition ^a	Transition energy, e.v.							
	Dqu	DquCoC ₅ H ₅		DquRhC ₅ H ₅		DquIrC ₅ H ₅		
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
$n-2b_{2g}$	2.78	2.8	2.8	3.0	3.0	3.6	3.5	
Metal- $2b_{2g}$		3.22	3.15	3.39	3.45	4.0	4.0	
$b_{3g}-2b_{2g}$	3.65	4.10	4.08	4.85	4.70	5.34	5.05	
$2b_{1u}-2b_{2g}$	4.62	5.00	5.00	5.57	5.60	5.40	5.72	

^a The group theoretical notation for the quinone orbitals is maintained for simplicity.

Experimental

The electronic spectra were obtained with a Perkin-Elmer instrument, Model 4000A.

Reaction of Rhodium Trichloride with Duroquinone.—Rhodium trichloride trihydrate (2.0 g.) and duroquinone (4.0 g.) were refluxed in 100 ml. of ethanol for 3 hr. The resulting dark red solution was evaporated *in vacuo* and the solid residue washed with hot benzene and ethanol. The resulting red powder, 0.8 g. (complex III), was washed several times with methanol and benzene and dried.

Anal. Calcd. for $C_{10}H_{12}O_2RhCl$: C, 39.7; H, 4.0; Rh, 34.0. Found: C, 39.1; H, 4.1; Rh, 32.3.

The infrared spectrum showed the quinone carbonyl bands at 1625 and 1600 cm^{-1} , respectively. The ethanol extracts were cooled and filtered to give 1.5 g. of durohydroquinone, m.p. 238°. The filtrate was concentrated, adsorbed on a column of unactivated silica gel, and eluted with 30% methanol-benzene to give very small amounts of a rose-colored material, soluble only in water or alcohol. For purification it was dissolved in the smallest quantity of methanol and precipitated by adding dry ether.

Anal. Found: C, 28.0; H, 3.6; Cl, 19.2; Rh, 42.3. This corresponds to $C_{11.4}H_{17.6}Rh_{2.6}Cl_{2.6}$, or $DquRh_2Cl_{2.6}$. The n.m.r. spectrum (in methanol) shows a sharp resonance at τ 8.25.

Reaction of III with Pyridine.—Compound III (250 mg.) was added to a mixture of 2.0 ml. of pyridine in 25 ml. of methylene chloride. The solution was evaporated, adsorbed on a column of silica gel, and eluted with 4% methanol-methylene chloride to give 235 mg. of an orange crystalline solid (IV), m.p. 280° dec.

The material was purified by dissolution in chloroform and precipitation with carbon tetrachloride.

Anal. Calcd. for $C_{20}H_{22}RhClO_2N_2$: C, 52.1; H, 4.8; Cl, 7.7; N, 6.1; O, 6.9; mol. wt., 461. Found: C, 54.3; H, 4.9; Cl, 7.0; N, 6.0; O, 7.0; mol. wt., 311.

The infrared spectrum (KBr) showed the quinone carbonyl stretching vibration at 1639 and 1600 cm^{-1} . In methylene chloride the duroquinone n.m.r. signal appeared at τ 8.40 and indicated the presence of pyridine. In the ultraviolet and visible range, absorption maxima occurred in chloroform at 510 (800), 455 (1200), 332 (5600), and 269 (13,000) $m\mu$.

Duroquinonecyclopentadienylrhodium (V).—Compound III (230 mg.) was covered with 20 ml. of dry tetrahydrofuran under N_2 and treated with 1.0 ml. of 1.3 *M* NaC_5H_5 solution in tetrahydrofuran. The reaction mixture was allowed to stand 1 hr. and was then evaporated *in vacuo*. The residue was recrystallized from dry tetrahydrofuran to give 190 mg. of product, m.p. 195° dec.

Anal. Calcd. for $C_{15}H_{17}O_2Rh$: C, 54.3; H, 5.1; Rh, 31.0; mol. wt., 332. Found: C, 54.1; H, 5.3; Rh, 31.8; mol. wt., 319.

Complex V can be sublimed above 160° under high vacuum. It is very soluble in chlorinated hydrocarbon solvents and in water, slightly soluble in benzene and tetrahydrofuran. It is a nonelectrolyte in nitrobenzene.

The infrared spectrum (KBr) shows, in addition to the carbonyl bands at 1580 and 1532 cm^{-1} , absorptions characteristic of the complexed duroquinone molecule; the bands at 3080, 1430, 1122, 1025, and 819 cm^{-1} correspond to the C_5H_5 ring system. The n.m.r. spectrum in chloroform shows two resonances at τ 4.75 and 7.85 in the ratio of 5:12. Expansion of the C_5H_5 proton resonance at 4.75 reveals a doublet ($J = 1.1$ c.p.s.). The absorption spectrum in the visible and ultraviolet range shows band maxima at 422 (300), 362 (9500), 262 (26,000), and 222 (18,000) $m\mu$ in H_2O .

Reaction of Iridium Trichloride with Duroquinone.—Iridium trichloride trihydrate, 2.0 g., was refluxed with 4.0 g. of duroquinone in 100 ml. of ethanol for 2 hr. and allowed to stand overnight. After filtration from very small amounts of a red complex (*vide infra*), the alcoholic solution was concentrated, adsorbed on a column of silica gel, and eluted with 20% methanol-benzene to give 1.25 g. of the lavender complex VI.

Anal. Found: C, 24.8; H, 2.7; Cl, 15.9; Ir, 50.7. This roughly corresponds to the composition $DquIrCl_2H$.

The infrared spectrum shows two C=O stretching bands at 1660 and 1600 cm^{-1} . In the n.m.r. spectrum one sharp signal is found at τ 8.15. The ultraviolet spectrum shows absorptions at 258 (6000), 309 (2000), 400 (700), 415 (750), and 485 $m\mu$ (450). The material is a weak acid and may be titrated with NaOH: calcd. equiv. wt., 428; found, 490; estimated $pK_a \sim 5$. During the titration a red precipitate (VII) formed which did not contain sodium or chlorine.

Anal. Calcd. for $C_{10}H_{13}O_3Ir$: C, 32.1; H, 3.5; Ir, 51.5. Found: C, 31.5; H, 3.4; Ir, 54.3.

The infrared spectrum is very similar to that of VI but contains an additional band at 2225 cm^{-1} . The complex dissolves in excess NaOH.

Filtration of the original reaction mixture afforded very small amounts of a crystalline complex of approximate composition Dqu_2IrCl_2H .

Anal. Calcd. for $C_{20}H_{26}IrO_4Cl_2$: C, 40.5; H, 4.1; Ir, 32.5. Found: C, 37.8; H, 4.2; Ir, 34.8.

This complex is probably a molecular addition compound of duroquinone with $DquIrCl_2H$. When heated in water it splits off duroquinone. When treated with pyridine, $DquIrPy_2Cl$ (complex X) is formed. This shows that at least one duroquinone is π -bonded.

Reaction of Complex VI with Hydrogen Iodide.—Complex VI was dissolved in distilled water and a few drops of 60% hydrogen iodide were added. The orange product (VIII) was filtered, washed with water, methanol, and methylene chloride, and dried.

Anal. Calcd. for $C_{10}H_{13}O_2IrI_2$: C, 19.7; H, 2.1; Ir, 31.5; I, 41.5. Found: C, 20.1; H, 2.4; Ir, 30.2; I, 41.5.

The infrared spectrum of this material is very similar to that of the chloro compound except that a singlet carbonyl frequency at 1590 cm^{-1} is observed.

Reaction of Complex VI with Tetramethylammonium Iodide.—Treatment of VI with tetramethylammonium iodide in water gave an orange crystalline precipitate (IX), which after filtration was washed with water and dried.

Anal. Calcd. for $C_{14}H_{24}O_2I_2N$ Ir: C, 24.5; H, 3.5; N, 2.0; Ir, 28.2. Found: C, 24.5; H, 3.7; N, 2.1; Ir, 28.4.

Reaction of Complex VI with Pyridine.—Compound VI (300 mg.) was dissolved in 50 ml. of pyridine under nitrogen and stripped *in vacuo*. The residue was adsorbed on a column of silica gel and eluted with 5% methanol-methylene chloride to give 240 mg. of red crystals (X), m.p. 180° dec. For analysis the material was recrystallized from methylene chloride-benzene.

Anal. Calcd. for $C_{20}H_{22}O_2N_2Cl$ Ir: C, 43.6; H, 4.0; N, 5.1; Cl, 6.4; Ir, 35.1; mol. wt., 550. Found: C, 44.1; H, 3.8; N, 5.1; Cl, 6.2; Ir, 35.0; mol. wt., 426.

The material is thermochromic, being red at room temperature and yellow at -75° . It is an electrolyte in water ($\lambda_m = 18$), but a nonelectrolyte in nitrobenzene. It did not give a precipitate with sodium tetraphenylboron.

The n.m.r. spectrum in methylene chloride exhibits the duroquinone proton signal at τ 8.85. The pyridine resonances appear in the range τ 2-2.5 and correspond to two molecules of pyridine per molecule of duroquinone. In the infrared spectrum quinone carbonyl bands are found at 1623 and 1600 cm^{-1} .

Duroquinonecyclopentadienyliridium (XI).—Compound VI (340 mg.) was covered with 20 ml. of dry tetrahydrofuran under nitrogen and heated with 2.0 ml. of a 1.3 *M* solution of NaC_5H_5 in tetrahydrofuran. After 1 hr. the reaction mixture was evaporated *in vacuo*, dissolved in 30 ml. of methylene chloride, filtered, and evaporated to give 185 mg. of cream-colored product, m.p. 315° dec. For analysis the complex was recrystallized from dry tetrahydrofuran.

Anal. Calcd. for $C_{15}H_{17}O_2Ir$: C, 42.8; H, 4.0. Found: C, 43.1; H, 4.3.

The n.m.r. data and the ultraviolet spectrum are described in the Discussion section. In the infrared spectrum, in addition to bands characteristic for the complexed C_5H_5 ring at 3090, 1408, 1122, 1028, and 830 cm^{-1} , the bands of the duroquinone system may be observed. The carbonyl stretching frequencies appear at 1590 and 1545 cm^{-1} .

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