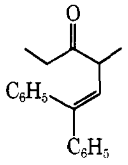
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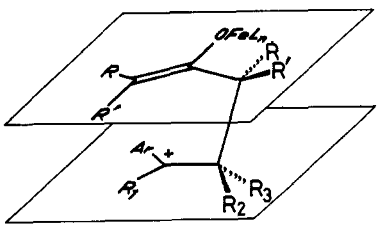
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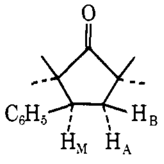
$Fe_2(CO)_9$.[9] Although the complex formation would assist the reaction by bringing the reactants in close proximity, the yield of the adducts does not necessarily correlate to the ease of the complex formation but appears to depend on the substituents affecting the stability of the carbocations. The reaction between α-cyclopropylstyrene and **1a**, which proceeds *via* the cationic species **5** stabilized by both phenyl and cyclopropyl groups, is remarkably smooth (95% yield). Competition experiments revealed that the reaction of α-methylstyrene with **1a** (benzene, 60°, <10 min) takes place approximately five times faster than that of unsubstituted styrene. The reaction using a 1:1 mixture of styrene and *trans*-β-methylstyrene as an olefinic substrate afforded only the styrene adduct. These results imply that the reaction rate is also sensitive to steric environment around the carbon–carbon double bond.

Particularly noteworthy is the fact that aryl-substituted olefins enter into the cycloaddition in a *stereospecific* manner and with retention of configuration. The dibromide **1c** (2 mmol) was mixed with a stirred suspension of $Fe_2(CO)_9$ (1 mmol) in benzene at 50° under nitrogen. After a 15-min reaction, *cis*-β-deuteriostyrene (2 mmol, prepared from deuteriophenylacetylene and disiamylborane) was added, and the resulting mixture was maintained at the same temperature for an additional 1 hr. Usual work-up followed by glpc purification gave the cyclopentanone **6**-*d*, mp 43–45°, in 10% yield.[10] The structure was firmly established by nmr analysis. The spectrum of the undeuterated adduct **6** (CCl_4, 100 MHz) exhibited a typical ABM multiplet centered at δ 1.9 (H_A), 2.2 (H_B), and 3.1 (H_M) ($J_{AB} = J_{BM} = 9.9$ Hz and $J_{AM} = 7.2$ Hz), while the spectrum of **6**-*d* displayed two broad doublets at δ 1.89 and 3.10 due to H_A and H_M ($J_{AM} = 7.2$ Hz), respectively.[11] Although stereospecificity of cycloaddition reaction has been used as a criterion of the concertedness,[12] the observed stereochemical result could be attributed to the rapid ring closure of the intermediate **5** or else its conformational integrity resulting from a charge-transfer interaction.[13]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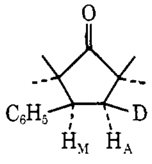
6-*d*

Acknowledgment. Financial support from the Matsunaga Science Foundation is acknowledged.

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[10] When the styrene was present in the reaction system from the beginning of the reduction, its cis–trans isomerization induced by $Fe_2(CO)_9$ occurred, though the cyclopentanone adduct was obtained in much improved yield.

[11] The dideuteriocyclopentanone 6-*3,4-cis-d*$_2$ (prepared by (1) aldol cyclization of 3,3,5-trimethyl-1-phenylhexane-1,4-dione with 10% CH_3ONa-CH_3OH (25°, 12 hr), (2) dehydration with 85% H_3PO_4 (120°, 20 min), and (3) catalytic deuteration over 10% Pd–C in *n*-hexane (atmospheric pressure, 25°, 4 hr)) gave a broad signal at δ 2.20 due to H_B.

[12] However, see N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1941 (1972), and papers in this series.

[13] Certain transition metals are known to remove the orbital-symmetry restrictions in pericyclic reactions [review: F. D. Mango and J. H. Schachtschneider, "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971, p 223]. The exact role of Fe atom or ion in the dibromo ketone–$Fe_2(CO)_9$ reactions is not yet known, but no apparent perturbations on the reaction mode have been observed.[7] For the reaction of 2 with 1,3-dienes forming 4-cycloheptenones, see R. Noyori, S. Makino, and H. Takaya, *J. Amer. Chem. Soc.*, **93**, 1272 (1971).

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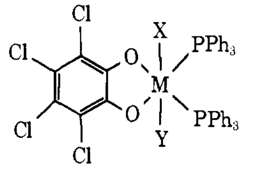
Oxidation of *o*-Quinone Adducts of Transition Metal Complexes

Sir:

Oxidative addition of *o*-quinones to a variety of low-valent metal complexes has attracted recent attention. Quinone additions to metals with formal d^{10},[1–5] d^8,[1,2,6] d^6,[6,7] d^4,[8] and d^2[9] electronic configurations have been reported. However, it has not been previously recognized that these complexes undergo a number of well defined, one-electron transfer reactions.

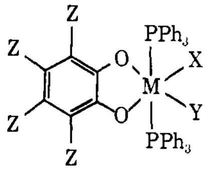
In particular complexes obtained from tetrahalobenzoquinones undergo one-electron oxidation to give complexes whose properties are indicative of the presence of coordinated semiquinone radicals. These oxidations have been detected by cyclic voltammetry which reveals that electron transfer in each case is reversible. Oxidative peak potentials ($E_p{}^{ox}$) for complexes **1–6** are set out in Table I. In addition the ruthenium complexes **5** and **6** undergo a second reversible one-electron oxidation at +1.7 V.



1, M = Pd; X,Y = nothing

2, M = Pt; X,Y = nothing

3, M = Ir; X = Cl; Y = CO



4, M = Rh; X = Cl; Y = CO; Z = Cl

5, M = Ru; X,Y = CO; Z = Cl

6, M = Ru; X,Y = CO; Z = Br

These oxidations may also be effected chemically with either of the oxidants—$NiS_4C_4(CF_3)_4$[10] or silver

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Table I. Polarographic Data for Neutral Complexes and Electron Spin Resonance Data for Cations

No.	Compound	E_p^{ox},[a] V	$\langle g \rangle$	$\langle A_{^{31}P} \rangle$, G
1	$Pd(o\text{-}O_2C_6Cl_4)(PPh_3)_2$	+0.73	2.006	<6[b]
2	$Pt(o\text{-}O_2C_6Cl_4)(PPh_3)_2$	+0.89	2.004	<8[b]
3	$Ir(o\text{-}O_2C_6Cl_4)(CO)Cl(PPh_3)_2$	+0.92	2.002	<8[b]
4	$Rh(o\text{-}O_2C_6Cl_4)(CO)Cl(PPh_3)_2$	+0.92	2.003	19.3
5	$Ru(o\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2$	+0.65	2.004	24.5
6	$Ru(o\text{-}O_2C_6Br_4)(CO)_2(PPh_3)_2$	+0.65	2.007	24.7

[a] In dichloromethane solution with $(C_4H_9)_4NPF_6$ as supporting electrolyte *vs.* an aqueous saturated calomel electrode. [b] Peak to peak line width.

hexafluorophosphate. For example treatment of an orange dichloromethane solution of **6** (λ_{max} 440 nm (ϵ 3.1 × 10^3), 330 (4.9 × 10^3); $\nu_{C\equiv O}$ 2046, 1994 cm^{-1}) with silver hexafluorophosphate produces a purple solution of the cation **6**$^+$ (λ_{max} 595 nm (ϵ 4.1 × 10^3), 518 (4.5 × 10^3), 415 (4.2 × 10^3), 385 (4.3 × 10^3), 335 sh (5.7 × 10^3); $\nu_{C\equiv O}$ 2074, 2023 cm^{-1}). The reaction to form **6**$^+$ is chemically reversible; reduction of a dichloromethane solution of **6**$^+$ with zinc quantitatively regenerates the electronic spectrum of **6**. Solutions of **6**$^+$ exhibit an esr spectrum consistent with a doublet ground state. Similar data have been obtained for the other complexes. However, because of the strongly oxidizing nature of the cations, no attempts have been made to isolate them. Due to the lower stability of the bonding between first-row transition metals and dioxylene ligands, the electron-transfer reactions of complexes of the type $M(o\text{-}O_2C_6Cl_4)_2{}^{2-}$ (M = Co, Ni, Cu) are significantly less well delineated.[11]

The formulation of the cations with the unpaired electron residing primarily on the dioxylene ligand rather than the metal is based on the following observations. The presence of a dioxylene ligand is necessary in order to observe reversible one-electron oxidations in such complexes (*e.g.*, $Pt(o\text{-}O_2C_6Cl_4)(PPh_3)_2$ undergoes this oxidation whereas $(Ph_3P)_2PtCl_2$, $(Ph_3P)_2Pt(PhC\equiv CPh)$, and $(Ph_3P)_2Pt(CS_2)$ do not). The isotropic *g* values for the various cations (Table I) are all quite similar with little dependence on the metal and are close to the isotropic value of 2.0054 reported[12] for a number of chlorinated *p*-quinones. Additionally the *g* tensor anisotropy for these cations is quite small; **5**$^+$ in dichloromethane at 77°K exhibits axial symmetry with $g_\perp = 2.020$ and $g_\parallel = 2.000$. These values contrast sharply with those observed for ruthenium(III)–phosphine compounds and other low-spin d^5 complexes which typically exhibit rhombic symmetry with $g_1 \sim 2.8$, $g_2 \sim 2.0$ and $g_3 \sim 1.6$.[13] Moreover spin-lattice relaxation is generally rapid for low-spin d^5 ions and consequently esr spectra of Ru(III), Ir(IV), and Rh(IV) species are generally only observable at low temperatures, whereas the esr spectra set out in Table I were obtained in solution at 25°.

Additionally these cations exhibit hyperfine coupling to the phosphine ligands which is sensitive to and diagnostic of the coordination geometry. Complexes **1**, **2**, and **3** have been shown to possess phosphine ligands which are trans to the dioxylene ligand.[2,6] No hyperfine splitting due to phosphorus is seen in the corresponding cations **1**$^+$, **2**$^+$, or **3**$^+$. However **4** has phosphines which are trans to one another and which lie above and below the dioxylene plane.[6] The esr spectrum of **4**$^+$ exhibits hyperfine splitting due to two equivalent phosphorus nuclei. The coordination geometry of **5** and **6** have not previously been determined. However, the observation of two infrared active carbonyl stretching frequencies in the neutral complexes[7] and in their respective cations indicates that the carbon monoxide ligands are cis to one another. The presence of hyperfine splitting by two equivalent phosphorus nuclei in the esr spectra of **5**$^+$ and **6**$^+$ along with the observation of two carbonyl stretching vibrations for each requires that the phosphines in these two complexes lie trans to each other and consequently the geometry of **5** and **6** is as depicted. The pattern of phosphorus hyperfine coupling is also consistent with the localization of the odd electron in these cations in a π orbital of the dioxylene ligand. When a phosphine lies trans to the dioxylene ligand the phosphorus s orbitals lie in the nodal plane of molecular orbital containing the odd electron. Consequently first-order theory of hyperfine coupling predicts that there should be no splitting from such phosphines. However, phosphines which lie above and below the dioxylene plane do not lie on a nodal plane of the crucial ligand molecular orbital. Therefore spin density may be transmitted to the phosphorus either through the metal or *via* a direct, through space interaction.

The cations described herein are unusually clear cut examples of species containing radical ligands, although it should be noted that coordination of semiquinones and semidiones by nontransition metal ions has also been detected.[14] A direct comparison of these complexes with their thio counterparts—the dithiolenes, which undergo extensive series of redox reactions[15]—cannot be made at this time since analogous dithiolene complexes of the heavier transition metals have not been synthesized. In general, however, the dithiolenes exhibit more extensive mixing of ligand and metal orbitals than observed here.

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[8]Annulene as a Neighboring Group. I. Multiple Rearrangement Attending the Solvolysis of Cyclooctatetraenylcarbinyl Chlorides

Sir:

Although cyclooctatetraene (**1**) occupies a central position as the smallest stable member of the nonaromatic annulenes, the literature fails to record a single experiment designed specifically to assess the capability of **1** to function as a neighboring group in solvolytic processes. The present study, an outgrowth of our interest in this question, provides relevant data that the ionization of cyclooctatetraenylcarbinyl de-