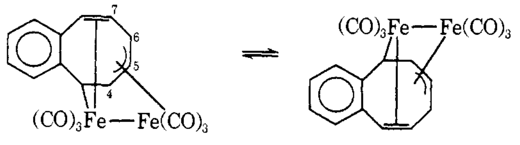
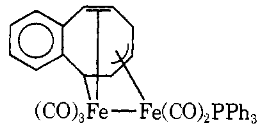


3

centered at δ 3.93 and 1.69 ($\nu_{1/2}$ = 8 Hz at −125°). An E_a of 8.1 kcal/mol may be calculated from these data. A "twitch" mechanism involving neither valence isomerism of the polyene ligand nor interconversion of the iron tricarbonyl groups is compatible with these data. The *mono*-triphenylphosphine derivative 4, prepared



4

from 3 and triphenylphosphine in cyclohexane at 100°, possesses a time-averaged plane of symmetry[11] (nmr equivalence of H-3 and H-8) with the phosphine residing on the iron furthest from the aromatic ring (P-H coupling[12] of H-5–H-6 but not of H-3–H-8). Of two alternative mechanisms considered[13] for dimetal hexacarbonyl isomerizations of this type, only the above twitch process is possible for 4. By inference this is true of 3 also.[14,15]

---

(11) The insolubility of 4 precluded low-temperature spectra.

(12) H. Brunner and E. Schmidt, *Angew. Chem.*, 87, 570 (1969).

(13) F. A. Cotton, D. G. DeBoer, and T. J. Marks, *J. Amer. Chem. Soc.*, 93, 5069 (1971).

(14) The question of any intermediates involved is of course open.

(15) Partial support by the National Science Foundation.

(16) National Institutes of Health Predoctoral Fellow, 1968–1971.

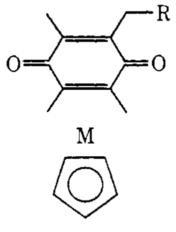
H. W. Whitlock, Jr.,* H. Stucki[16]
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received June 8, 1972

Organic Chemistry of Transition Metal Ligands. I. Duroquinone

Sir:

π ligands which undergo electrophilic substitution are well known, the cyclopentadienyl rings of ferrocene and cymantrene being prime examples. Likewise, a number of unstable or unreactive π ligands have been found to undergo substitution reactions when complexed by a transition metal. Electrophilic substitution of π-cyclobutadieneiron tricarbonyl[1] and π-cyclooctatetraeneiron tricarbonyl[2] serves as an example of a process whereby derivatives of unstable organic molecules as ligands are prepared, while electrophilic substitution of a cobalt cluster complex of tolan[3] and a two-step sequence, which amounts to nucleophilic substitution of an allylic position of a series of cyclopentadienyl(cycloocta-1,5-diene)metal complexes (metal = Co, Rh, Ir),[4] serve as examples of transformations of unreactive organic molecules as ligands. However, no example of a relatively general activation of the ability of a saturated carbon atom in a π complex to undergo both acid- and base-catalyzed substitutions and condensations has ever been reported. We now now describe a series of such molecules, namely, cyclopentadienylduroquinone cobalt, rhodium, and iridium (**1a–c**).[5]



1a, M = Co; R = H
b, M = Rh; R = H
c, M = Ir; R = H
2a, M = Co; R = $CH_2N(CH_3)_2$
b, M = Rh; R = $CH_2N(CH_3)_2$
c, M = Ir; R = $CH_2N(CH_3)_2$
3a, M = Co; R = $CH_2N(CH_3)_3{}^+I$
b, M = Rh; R = $CH_2N(CH_3)_3{}^+I$
4a, M = Co; R = CH_2OCH_3
b, M = Rh; R = CH_2OCH_3

Complexes **1a–c** were demonstrated to undergo a variety of substitution reactions. Dimethylaminomethylation (Mannich conditions) of **1a–c** produced the derivatives **2a–c** in which substitution of a methyl hydrogen had occurred in yields of 90, 42, and 38%, respectively.[6,7] These dimethylaminomethyl derivatives were converted to their respective methiodides **3a–c**, each in *ca.* 98% yield. Methiodides **3a** and **3b** were also converted into the ethers **4a** and **4b** with sodium methoxide in benzene in each case with yields of 95%.[6]

Support for the structures proposed for these complexes rests primarily on their 100-MHz spectra and their mass spectra. For example, the nmr spectrum of dimethylaminomethyl derivative **2a** presented overlapping peaks at τ 7.95, 7.92, and 7.88 (nine protons) which were assigned to the three ring methyls. Signals at τ 7.74–7.21 (total ten protons) and a singlet at 5.23 (five protons) were assigned to the two methylene groups, the *N*-methyls and the unsubstituted cyclopentadienyl ring, respectively. Spectra of **2b** and **2c** were very similar to that of **2a**. Similarly, the mass spectrum of complex **2a** provided distinct evidence as to the assigned structure. Positive fragments characteristic of C_5H_5 (*m/e* 65), C_5H_5Co (*m/e* 124,) $C_{11}H_{12}O_2$ (*m/e* 176), and the molecular ion, $C_5H_5CoC_{13}H_{19}NO_2$ (*m/e* 345), were found in high abundances. The spectrum of **2b** was more complex, notably in exhibit-

---

(1) R. G. Amiet and R. Pettit, *J. Amer. Chem. Soc.*, 90, 1059 (1968).

(2) B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc. A*, 422 (1971).

(3) D. Seyferth and A. T. Wehman, *J. Amer. Chem. Soc.*, 92, 5520 (1970).

(4) (a) J. Lewis and A. W. Parkins, *J. Chem. Soc. A*, 1150 (1967); (b) J. Lewis and A. W. Parkins, *ibid.*, 953 (1969).

(5) G. N. Schrauzer and H. Thyret, *Angew. Chem.*, 75, 641 (1963); G. N. Schrauzer and K. C. Dewhirst, *J. Amer. Chem. Soc.*, 86, 3265 (1964).

(6) Elemental analyses of complexes **3a**, **2b**, **3a**, **3b**, and **4b** revealed the presence of varying amounts of water of hydration, but were otherwise acceptable.

(7) A thorough search of the literature has revealed no example of an organic reaction which allows derivatization of duroquinone at a methyl group. Furthermore, R. Marchal of these laboratories has duplicated the Mannich conditions used for complex **1a** on duroquinone itself. A crude product was obtained after chromatographic removal of duroquinone (*ca.* 30%) that by nmr analysis obviously no longer contained a quinoid structure.

ing an ion which could be assigned to the substituted moiety $C_{13}H_{19}NO_2$ (*m/e* 221). In addition, ir spectra of complexes **2a** and **2b** exhibited absorptions at 1100 and 1000 cm^{-1} which are characteristic of an unsubstituted cyclopentadienyl ring π bonded to a metal.[8] Nmr and ir data of a similar nature in support of the structures **3a,b** and **4a,b** were also obtained.

The electrophilic reactivity of the methyl groups of complexes **1a–c** suggested the possibility of realization of base-catalyzed reactions. Complex **1a** was condensed with benzaldehyde in sodium methoxide–ethanol resulting in a mixture of condensation products. These could not be completely separated by chromatography but sufficient fractionation was achieved that nmr analysis (phenyl *vs.* unsubstituted methyl signals) permitted the conclusion that mono, di, tri, and tetra condensation products had been formed. A precise demonstration of the base-catalyzed reactivity of these complexes is provided by the observation that complex **1b** underwent significant deuterium exchange with sodium deuteroxide–methanol-d_1 after stirring at room temperature for 12 hr. The deuterium content of the resulting complex was measured by two independent techniques. Assuming that no deuterium exchange had occurred at the cyclopentadienyl ring, comparison by nmr of the integrated intensities of the cyclopentadienyl ring protons and the remainder of the signal for the duroquinone methyl groups indicated that 10.6 atoms of deuterium had been incorporated. Chemical analysis for deuterium content by the falling drop method[9] indicated that *ca.* 10.9 atoms of deuterium were present in the molecule as a whole. Comparison of these two results permitted the conclusion that no significant deuterium exchange had occurred in the cyclopentadienyl ring and that essentially the total deuterium content resided in the methyl groups of the duroquinone ligand. This is a most provocative conclusion since duroquinone itself does not undergo any exchange under these same conditions.[10]

It is appropriate to conclude that π complexation to a transition metal activated the methyl groups of duroquinone toward both acid- and base-catalyzed reactions in an extraordinary manner. This activation promises to be of considerable importance since it demonstrates the potential that complexation of an organic ligand by a transition metal may be useful in the synthesis of previously difficult to obtain or unattainable compounds if the substituted ligand can be removed intact from the metal.[11,12] Experiments designed to demonstrate this last step in the synthesis of substituted duroquinones are under examination.

Acknowledgment. Support by the Office of Research and Projects, Southern Illinois University, is gratefully acknowledged. T. R. E. was a NASA Fellow, 1966–1969.

D. W. Slocum,* T. R. Engelmann
Neckers Laboratory, Southern Illinois University
Carbondale, Illinois 62901

Received June 14, 1972

---

[8] H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 240 (1964).

[9] Joseph Nemath, University of Illinois, Urbana, Ill.

[10] A. Lapidot, B. L. Silver, and D. Samuel, *Biochem. Biophys. Res. Commun.*, **21**, 126 (1965).

[11] Four examples of this overall procedure have been reported. Substitution reactions of cyclobutadiene have been described by R. Pettit and coworkers [J. S. Ward and R. Pettit, *J. Amer. Chem. Soc.*, **93**, 262 (1971), and references cited therein] and mesitylene by J. F. Helling and D. M. Braitsch, *J. Amer. Chem. Soc.*, **92**, 7207 (1970); *cf.* also ref 2 and 3.

[12] Mr. R. Marchal has decomposed complex **1a** by use of aqueous ceric ammonium nitrate with recovery of 90% of the duroquinone. In the one instance where a derivatized complex has been decomposed by this technique, **2a** has afforded 2-(*N*,*N*-dimethylaminoethyl)-3,5,6-trimethyl-1,4-benzoquinone as an oil in 58% yield; nmr τ 7.62 and 755 (overlapping singlets), 7.26 (s), and 7.25–6.5 (m) in relative areas of 9:6:4, respectively.

Cyanoborane Chemistry. I. Preparation of a Novel Series of Macrocyclic Cyanoboranes[1]

Sir:

The existence of cyanoborane, BH_2CN, as a stable monomer under ordinary conditions is unlikely. Conceptually, these moieties could undergo association in a number of ways, one being the formation of a coordinate covalent bond by the donation of a nitrogen atom's lone pair of electrons into an empty boron orbital. The result of such a process would be the formation of linear and/or cyclic polymers. Assuming a 180° configuration for difunctional cyanide, four atom BCNB rods would result. Some of the macrocyclic molecules which might be expected are depicted in Figure 1. We wish to report in this communication evidence for a series of macrocyclic oligomers of cyanoborane, $(BH_2CN)_n$, with $n = 4–9$.

A suspension of sodium cyanotrihydroborate, $NaBH_3CN$,[2] in dry diethyl ether reacts with hydrogen chloride in a 1:1 ratio at ambient temperatures to yield a quantitative amount of hydrogen, sodium chloride, and, upon removal of the ether, polymeric cyanoborane. Up to 20% of this material is volatile under a vacuum of 10^{-5} Torr at room temperature and can be collected as a white crystalline solid. *Anal.* Calcd for $(BH_2CN)_n$: C, 30.91; H, 5.20; N, 36.06; B, 27.85. Found: C, 30.78; H, 5.25; N, 35.88; B, 27.87.

Analytical glc analysis of the volatile material using OV-17 on acid-washed Chromosorb W resulted in the elution of seven distinct components. Mass spectra obtained on the first five components exhibited sharp cutoffs in the spectra at *m/e* 156, 195, 234, 273, and 312. These peaks correspond to the molecular ion for $(^{11}BH_2CN)_n$, where $n = 4–8$. All of the fragmentation patterns show the familiar boron isotope and hydrogen loss effects. The mass spectrum for the sixth component was of low intensity due to insufficient sample and the highest peak observed was *m/e* 348 [*vs.* 351 expected for $(^{11}BH_2CN)_9{}^+$]. The fragmentation pattern, however, was similar to the others. No mass spectral data were obtained for the seventh component. Relative proportions of the volatile cyanoboranes eluted by glc from a typical run are as follows: 3% $(BH_2CN)_4$, 87% $(BH_2CN)_5$, 8% $(BH_2CN)_6$, 1% $(BH_2CN)_7$, traces of $(BH_2CN)_8$, $(BH_2CN)_9$, and possibly $(BH_2CN)_{10}$.

By means of fractional sublimation, samples containing $(BH_2CN)_5$ in excess of 90% purity as determined by glc analysis could be obtained. The ^{11}B nmr spectrum of this material consists only of a 1:2:1 triplet at +28 ppm (J = 109 Hz) relative to $BF_3 \cdot Et_2O$. The appearance of the upfield triplet indicates that all of the

---

[1] Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971; and at the 163rd National Meeting, Boston, Mass., April 1972.

[2] Available from Ventron Corp., Chemical Division, Beverly, Mass.