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CYCLOBUTADIENE-METAL COMPLEXES (VII)* REACTIVITY OF π-COMPLEXED ORGANOMETALLIC CATIONS TO NUCLEOPHILIC ATTACK

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There have been numerous reports of the reactions of nucleophiles with π-complexed organometallic cations. However very few of them have dealt with nucleophilic attack on "sandwich" complexes containing two different organic ligands (1,2). A study of this type of system would allow a comparison of the ease, and direction, of addition to various ligands. We report here a comparison between three isoelectronic** cations which allows a generalization to be proposed concerning the ease of attack on different π-bonded rings.

We have already described the reaction of (π-cyclopentadienyl)-(π-tetraphenylcyclobutadiene) -nickel and -palladium bromides (I, M = Ni or Pd) with alkoxide ion (3). This facile reaction proceeds with attack of OR^- on the four-membered ring, exo- to the metal, to give the (π-cyclopentadienyl)(π-alkoxytetraphenylcyclobutenyl) -nickel and -palladium complexes (II, M = Ni or Pd).

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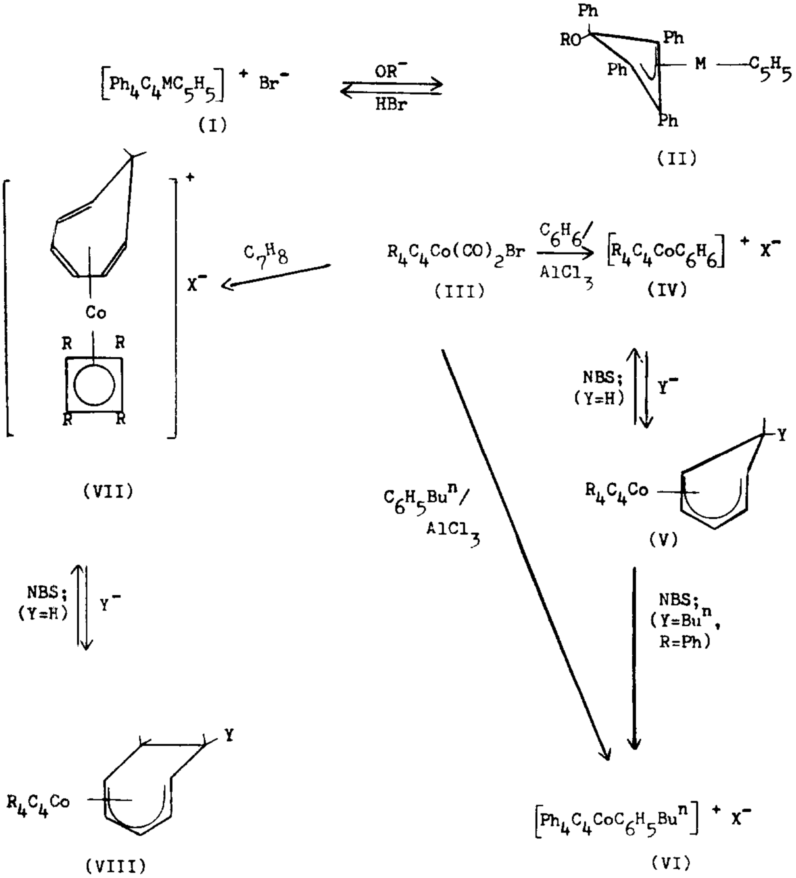
*Part (VI), Ref. 4

**The term "isoelectronic" is here taken to mean complexes having the same total number of metal valence-shell d-electrons and ligand π-electrons which are engaged in bonding to the metal.

By analogy with the synthesis of the (π-benzene)(π-tetraphenylcyclobutadiene)cobalt cation (IV) (4), bromodicarbonyl(tetraphenylcyclobutadiene)- cobalt(I) (III, R = Ph) reacted with cycloheptatriene on heating to give the (π-cycloheptatriene)(π-tetraphenylcyclobutadiene) cobalt(I) cation (VII). This was characterized as the iodide, hexafluorophosphate and tetrathiocyanatocobaltate(II) (VII, R = Ph, X = I, PF_6 and $\frac{1}{2}$ $[Co(NCS)_4]$) (5) and was obtained in 13-18% overall yield.



The π-benzene cation (IV) is reminiscent of the isoelectronic cobalticinium cation in stability (6); attack by nucleophiles is difficult and (IV) resists alkoxides and Grignard reagents. Butyllithium or borohydride however converted it into the (π-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt complexes (V, R = Ph, Y = Bu^n or H) (5) in 53% and 20% yield respectively. The H^1 NMR spectrum of (IV, R = Ph) showed two singlets, one at 2.5τ(Ph), the other at 3.35τ(C_6H_6), with relative intensities 20:6. On reduction to (V), the sharp singlet due to the π-complexed benzene disappeared (7). Further evidence that attack had occurred on the six-membered ring was obtained from the H^1 NMR spectra of the p-tolyl complexes (IV, R = p-$CH_3C_6H_4$, and V, R = p-$CH_3C_6H_4$, Y = Bu^n) (5). In both cases a sharp AB pattern in the phenyl region was obtained. We have shown (10) that whenever this is present all the phenyl groups present in the molecule are equivalent. Hence attack by the nucleophile here has not occurred on the cyclobutadiene ring.

The complexes (V, R = Ph, Y = H and Bu^n) were converted to (IV, R = Ph) and (VI) (5) respectively in 80% yield by the action of N-bromosuccinimide in methanol. This appears to be a general reagent for hydride-abstraction in these types of compounds, however, good yields are only obtained when the product cation is very stable. (VI) was also synthesized directly from (III, R = Ph) and n-butylbenzene in the presence of aluminum chloride.

The π-cycloheptatriene complexes (VII, R = Ph, p-$CH_3C_6H_4$) were, by contrast, very susceptible to nucleophilic attack. Alkoxides, borohydride, water in the presence of tert-amines, and even acetate ion, all reacted to give the π-cycloheptadienyl complexes (VIII, R = C_6H_5, Y = H, OH, OMe, $OCOCH_3$, and R = p-$CH_3C_6H_5$, Y = $OCOCH_3$) (5) in 16 - 65% yields. (VIII, R = C_6H_5, Y = H) was reconverted to (VII, R = C_6H_5) by N-bromosuccinimide in methanol, however only an 18% yield was obtained. Confirmation that nucleophilic attack occurred on the cycloheptatriene ring in (VII) was again obtained from the H^1 NMR spectrum of (VIII, R = p-$CH_3C_6H_4$, Y = $OCOCH_3$) (7). This showed a sharp AB splitting pattern of the phenyl protons and implied the continued equivalence of the four phenyl groups.

The observation that nucleophilic attack occurs with greater facility in the cycloheptatriene complexes (VII) than in the benzene complexes (IV) is not unexpected since it will obviously be a less favourable process to destroy the closed cyclic conjugation of the benzene ring than to add a nucleophile to the cycloheptatriene. Attack on the benzene ring rather than on the tetraphenylcyclobutadiene in (IV) is surprising, especially in view of the ease with which the four-membered ring in the isoelectronic complex (I, M = Ni and Pd) is attacked.

These results suggest that an order of reactivity of π-complexed organic ligands towards nucleophiles can be proposed, cycloheptatriene $>$ benzene $>$ tetraphenylcyclobutadiene $>$ cyclopentadienyl, the last being the most stable. Confirmation is provided by the observation that the (π-benzene)(π-cyclopentadienyl)iron cation undergoes attack on the benzene ring (1,11). Green and coworkers (2) have also shown that in cations such as dicarbonyl(ethylene)(cyclopentadienyl)iron, attack occurs on the ethylene rather than on the cyclopentadienyl group.

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REFERENCES

1. D. Jones, L. Pratt and G. Wilkinson, J. Chem. Soc., 4458 (1962).
2. M. L. H. Green and P. L. I. Nagy, J. Amer. Chem. Soc., 84, 1310 (1962); J. Organometallic Chem., 1, 58 (1963); M. Cousins and M. L. H. Green, J. Chem. Soc., 889 (1963); M. L. H. Green and A. N. Stear, J. Organometallic Chem., 1, 230 (1964).
3. P. M. Maitlis, A. Efraty and M. L. Games, J. Amer. Chem. Soc., 87, 719 (1965).
4. P. M. Maitlis and A. Efraty, J. Organometallic Chem., 4, 175 (1965).
5. Satisfactory analyses were obtained for all new compounds reported.
6. G. Wilkinson, J. Amer. Chem. Soc., 74, 6148 (1952).
7. Due to the complexity of the H^1 NMR spectra of the π-cyclohexadienyl and the π-cycloheptadienyl groups in the complexes (V) and (VIII), and to the low solubility of the compounds, it was not possible to interpret the spectrum fully. However, sufficient detail was observed to make the similarity to published spectra (1,9,10) of analogous complexes containing these ligands clear.
8. H. J. Dauben and D. J. Bertelli, J. Amer. Chem. Soc., 83, 497 (1961).
9. G. Winkhaus and G. Wilkinson, Proc. Chem. Soc., 311 (1960).
10. P. M. Maitlis, D. Pollock and A. Efraty, unpublished results. For example, in the tetrakis(p-tolyl)cyclobutenyl analog of (II), no AB pattern of the phenyl protons is observed. This supports the structure given.
11. The product from borohydride reduction of $\left[(C_5H_5)W(C_6H_6)CO\right]^{\oplus} PF_6^{\ominus}$ is probably $(C_5H_5)W(C_6H_8)(CO)H$ [E. O. Fischer and F. J. Kohl, Chem. Ber., 98, 2134 (1965)], attack again occurring on the benzene ring.