quite clear when it is noticed that the reported preparation[3] of h^5-$C_5H_5CuPEt_3$ from Cu_2O (cuprous oxide itself has no ability of metalation of cyclopentadiene), PEt_3, and cyclopentadiene required the reflux temperature of petroleum ether. The cuprous *tert*-butoxide–phosphine complex is assumed to be an active metalation species. **1** has a limited solubility in petroleum ether. However, addition of an equimolar amount of triethylphosphine gave a homogeneous solution. By sublimation at *ca.* 100° (1 mm), the *tert*-$BuOCuPEt_3$ complex **3** was isolated. The ir spectrum showed *tert*-butyl–O stretching vibration at 955 and 940 cm^{-1} (doublet). The nmr spectrum in deuterated benzene showed a singlet of the *tert*-butoxy group at τ 8.47 and a multiplet of triethylphosphine at near τ 9.00. Relative peak area was consistent with 1:1 complex of **3**. Copper content by iodometry was 26.6% (calcd 24.9%). By benzyl alcoholysis, **3** gave *tert*-butyl alcohol in a yield of 98%. On reaction with cyclopentadiene at *ca.* −70°, **3** gave smoothly h^5-$C_5H_5CuPEt_3$.

Reactions of **1**, **2**, and **3** with various functional groups as well as its catalysis behavior are being investigated.

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Oxidative Cleavage of Cobalt–Carbon Bonds in Organobis(dimethylglyoximato)cobalt Compounds

Sir:

The cleavage of cobalt–carbon bonds in organocobalt compounds is a subject of considerable current interest in a number of contexts including various homogeneous catalytic processes[1] as well as the chemistry and biological activity of vitamin B_{12} coenzymes.[2] Several modes of such cleavage have already been described, including homolysis,[3] photolysis,[4] and reductive dealkylation.[5] In this communication we describe still another pathway of cleavage of cobalt–carbon bonds which involves the initial one-electron oxidation of an organocobalt(III) compound.

Our observations relate to the oxidation of benzylaquobis(dimethylglyoximato)cobalt(III) (**1**), *i.e.*, $Co(DH)_2(H_2O)R$ (where DH_2 = dimethylglyoxime, *i.e.*, $HON{=}C(CH_3)C(CH_3){=}NOH$, and $R = C_6H_5CH_2$) by hexachloroiridate(IV). In dilute aqueous $HClO_4$ solution (0.1–1 *M*), with $IrCl_6^{2-}$ initially in excess over the cobalt complex, the reaction between $Co(DH)_2(H_2O)R$ and $IrCl_6^{2-}$ was found to proceed rapdly in accord with the stoichiometry depicted by eq 1. This stoichiometry was established by spectrophotometric titrations (confirming that **1** and $IrCl_6^{2-}$ react in the ratio 1:2 to form **2**) and by the quantitative (*ca.* 90%) isolation and characterization of the organic product, *i.e.*, $C_6H_5CH_2OH$.

$$\underset{\mathbf{1}}{Co(DH)_2(H_2O)R} + 2IrCl_6^{2-} + 2H_2O \longrightarrow \underset{\mathbf{2}}{Co(DH)_2(H_2O)_2^+} + 2IrCl_6^{3-} + ROH + H^+ \quad (1)$$

Assuming the usual role of a one-electron outer-sphere oxidant for $IrCl_6^{2-}$,[6,7] the overall reaction stoichiometry together with the results of preliminary kinetic measurements[8] and the further chemical evidence described below are plausibly accommodated by the following mechanism

$$Co(DH)_2(H_2O)R + IrCl_6^{2-} \xrightarrow{k} \underset{\mathbf{3}}{[Co(DH)_2(H_2O)R]^+} + IrCl_6^{3-} \quad (2)$$

followed by

$$\mathbf{3} + IrCl_6^{2-} + 2H_2O \longrightarrow Co(DH)_2(H_2O)_2^+ + ROH + IrCl_6^{3-} + H^+ \quad (3)$$

or, alternatively, by the stepwise free-radical sequence

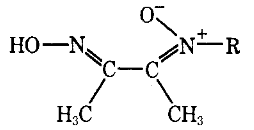
$$\mathbf{3} + H_2O \longrightarrow Co(DH)_2(H_2O)_2^+ + R\cdot \quad (4)$$

$$R\cdot + IrCl_6^{2-} + H_2O \longrightarrow ROH + IrCl_6^{3-} + H^+ \quad (5)$$

When $Co(DH)_2(H_2O)R$ was initially in excess over $IrCl_6^{2-}$, the overall stoichiometry of the reaction was altered. Under these conditions $Co(DH)_2(H_2O)R$ and $IrCl_6^{2-}$ reacted in the exact ratio 1:1 (confirmed by spectral titrations) to yield the products indicated in eq 6 together with a small amount (1–2%) of bibenzyl (R_2).

$$Co(DH)_2(H_2O)R + IrCl_6^{2-} + H^+ \longrightarrow IrCl_6^{3-} + H_2O +$$

$$Co^{2+} + DH_2 + \quad (6)$$



4

The organic product **4** (mp 85–86°) was isolated in quantitative yield by ether extraction of the product solution, followed by silica gel column chromatographic separation from the DH_2 product (which was also recovered quantitatively) and from the traces of bibenzyl. The structural assignment of **4** is based upon its correct elemental analysis and mass spectrometric molecular weight and upon the following spectral properties: nmr ($CDCl_3$) δ 7.3 (5 H, s, C_6H_5), 5.16 (2 H, s, CH_2), 2.03 (3 H, s, CH_3), 2.00 (3 H, s, CH_3),

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[1] J. Halpern, *Advan. Chem. Ser.*, **No. 70**, 1 (1968), and references cited therein.

[2] R. H. Abeles, *ibid.*, **No. 100**, 346 (1971), and references cited therein.

[3] J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, **86**, 2311 (1964).

[4] D. Dolphin, A. W. Johnson, and R. Rodrigo, *J. Chem. Soc.*, 3186 (1964).

[5] G. Costa, A. Puxeddu, and E. Reisenhofer, *Chem. Commun.*, 993 (1971), and references cited therein.

[6] J. Halpern, R. J. Legare, and R. Lumry, *J. Amer. Chem. Soc.*, **85**, 680 (1963).

[7] P. Abley and J. Halpern, *Chem. Commun.*, 1238 (1971).

[8] Simple limiting kinetics of the form $-d[Co(DH)_2(H_2O)R]/dt = k[Co(DH)_2(H_2O)R] - [IrCl_6^{2-}]$, consistent with reaction 2 being rate determining, were observed for $R = p\text{-}CH_3C_6H_4CH_2$ and $p\text{-}CH_3OC_6H_4CH_2$ ($k = 2 \times 10^5$ and 3×10^5 M^{-1} sec $^{-1}$, respectively.[9] For $R = C_6H_5CH_2$ and $p\text{-}FC_6H_4CH_2$, the kinetic behavior was more complex with some indication of competition from the back reaction of eq 2. Further investigations to elucidate the detailed kinetic behavior of these systems are in progress.

[9] An inverse dependence of the rate on the H^+ concentration was observed, similar to that recently reported[10] for the alkylation of Hg^{2+} by alkylbis(dimethylglyoximato)cobalt(III) complexes. This dependence, in both cases, is attributable to reversible protonation of one of the DH^- ligands to form an *inactive* $Co(DH)(DH_2)(H_2O)R^+$ complex. The values of k were determined by extrapolation to $[H^+] = 0$, in accord with the procedure of Adin and Espenson.[10]

[10] A. Adin and J. H. Espenson, *Chem. Commun.*, 653 (1971).

8.7 (1 H, broad, OH); uv max (CH_3OH), 231 nm (ϵ 2.4×10^4).[11]

Presumably, in the absence of excess $IrCl_6^{2-}$ to intercept the intermediate **3**, the latter decomposes in accord with eq 7 or, alternatively, by an equivalent stepwise mechanism involving the release of a benzyl radical (according to eq 4), which is subsequently trapped by one of the DH^- ligands of **3**. Some support for the suggestion that the latter alternative is at least a contributing pathway is provided by the accompanying formation of traces of bibenzyl.

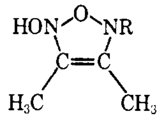
$$Co(DH)_2(H_2O)R^+ + H^+ \longrightarrow Co^{2+} + DH_2 + \mathbf{4} + H_2O \quad (7)$$

Para-substituted benzyl analogs of **1**, *i.e.*, $Co(DH)_2(H_2O)(p\text{-}CH_2C_6H_4X)$, were found to undergo analogous reactions with $IrCl_6^{2-}$, the reactivities increasing somewhat, as expected, with increasing electron-donating ability of X. With the cobalt compound initially in excess over $IrCl_6^{2-}$, the stoichiometry in each case corresponded to that of eq 6 and, in each case, an organic product, whose nmr spectrum, elemental analysis, and molecular weight were consistent with those expected for the corresponding para-substituted analog of **4**, was isolated in quantitative yield. With $IrCl_6^{2-}$ initially in excess over the cobalt complexes, the reactions of the para-substituted compounds exhibited stoichiometries intermediate between those of eq 1 and 6, the organic products being mixtures (ranging from *ca.* 1:2 to 2:1) of the para-substituted benzyl alcohols and the corresponding derivatives of **4** (together with equivalent amounts of DH_2). $Co(DH)_2(H_2O)(p\text{-}CH_2C_6H_4NO_2)$ reacted only very slowly with $IrCl_6^{2-}$. $Co(DH)_2(H_2O)(CH_3)$ was virtually unreactive.

Recent interpretations[12,13] of vitamin B_{12}-dependent reactions, such as the deamination of ethanolamine, have invoked mechanisms involving the homolytic cleavage of the cobalt–carbon bond of vitamin B_{12} coenzyme with formation of a 5′-deoxyadenosyl free radical which plays an important role in the catalytic transformation of the substrate. The observations described in this communication suggest another possible route (*i.e.*, oxidative dealkylation), in addition to those already considered, through which such radical-generating cobalt–carbon bond cleavage might occur.

Acknowledgment. We are grateful to Mr. Daniel Roberts for technical assistance and to the National Institutes of Health and the National Science Foundation for financial support.

(11) An alternative structural assignment, which is somewhat less readily reconciled with the uv spectral evidence but which cannot be excluded, is that of the closely related cyclic isomer of **4**, *i.e.*



It is planned to establish the structure conclusively by X-ray crystallography.

(12) B. M. Babior, *J. Biol. Chem.*, **245**, 6125 (1970).

(13) P. Y. Law, D. G. Brown, E. L. Lien, B. M. Babior, and J. M. Wood, *Biochemistry*, 10, 3428 (1971), and references cited therein.

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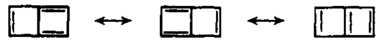
p-Benzyne. Generation as an Intermediate in a Thermal Isomerization Reaction and Trapping Evidence for the 1,4-Benzenediyl Structure

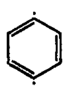
Sir:

We wish to report that *cis*-1,5-hexadiyn-3-ene (**2**) undergoes a striking thermal degenerate rearrangement which requires that it pass through, at least on the average, a species with a new C_2 symmetry axis; *i.e.* *p*-benzyne (**1**).[1] Furthermore, we have obtained evidence that **1** is a true intermediate with a lifetime long enough to allow trapping by external reagents. These trapping reactions suggest that **1** is best represented by the benzene-1,4-diyl structure[2] **1c**. Finally, our data also allow us to estimate a maximum heat of formation for this diradical.

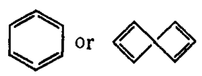


1a

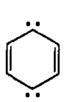
1b



1c

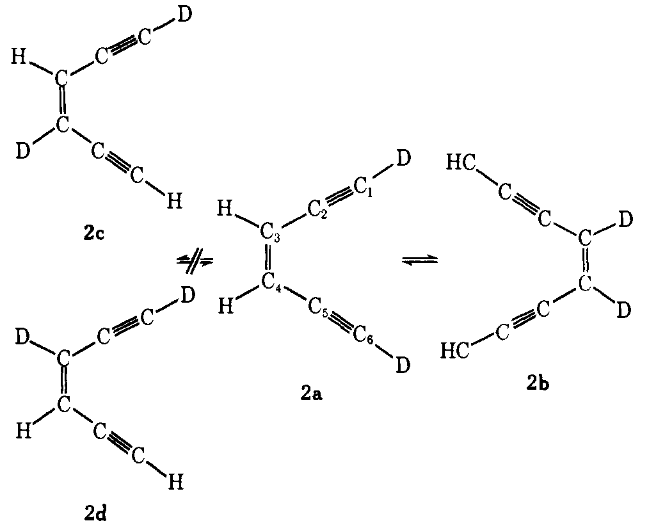


1d



1e

Reaction of 3-hydroxy-1,5-hexadiyne[3] with *p*-toluenesulfonyl chloride in pyridine and treatment of the tosylate with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in triethylene glycol-*O*-d_2, followed by reexposure of the products[4] to the deuterated medium, produced a 40:60 mixture of **2a** and its trans isomer **3**, >99% deuterated[5] in the acetylenic positions. Gas-phase pyrolysis in a flow system at 300° (atmospheric pressure, contact time



2c **2d** **2a** **2b**

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(1) (a) J. D. Roberts, A. Streitwieser, Jr., and C. Regan, *J. Amer. Chem. Soc.*, **74**, 4579 (1952); (b) M. J. S. Dewar and C. DeLlano, *ibid.*, **91**, 789 (1969); (c) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, 1003 (1965); (d) I. P. Fischer and F. P. Lossing, *J. Amer. Chem. Soc.*, **85**, 1018 (1963); (e) R. Hoyos de Rossi, H. E. Bertorello, and R. A. Rossi, *J. Org. Chem.*, **35**, 3328 (1970).

(2) (a) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); (b) M. D. Gheorghin and R. Hoffmann, *Rev. Roum. Chim.*, **14**, 947 (1969). A correlation diagram using the orbital energy arrangement for **1c** predicted by these workers[2a] suggests that the **2** $\rightleftharpoons$ **1c** interconversion is a symmetry-allowed process. Conversion of **2** into **1a** is predicted to be forbidden.

(3) F. Sondheimer, Y. Amiel, and Y. Gaoni, *J. Amer. Chem. Soc.*, **84**, 270 (1961).

(4) W. H. Okamura and F. Sondheimer, *ibid.*, **89**, 5991 (1967).

(5) Nmr analyses were performed on a Varian A60-A instrument. Mass spectral analyses were carried out on a gas chromatography–mass spectrometry apparatus employing Hewlett-Packard 7620A and EAI Quad-300 instruments.