effective perturbation method to the EHMO results. The broken curves give the results derived from the point charge calculations for two different choices of the radial parameter[10] ρ_2. The quantitative agreement between the two theories is gratifying and suggests that the present method represents a viable alternative to electrostatic crystal or ligand field theory. Furthermore it provides a practical means of testing semiempirical MO theories against many electron spectral and magnetic properties in complexes.

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[10] $\rho_2 = \langle r^2\rangle/R^3$; $\rho_4 = \langle r^4\rangle/R^5$, where R is the metal to point charge distance.

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Cuprous *tert*-Butoxide. A New and Useful Metalation Reagent

Sir:

This communication reports the interesting properties and metalation reactivity of cuprous *tert*-butoxide (**1**) which differs very much from cuprous alkoxides reported. Among the very few cuprous alkoxides studied, cuprous methoxide is known to be quite insoluble in organic solvents and unstable.[1] It decomposes at room temperature, sometimes explosively, into formaldehyde, methanol, and metallic copper.[1] On the contrary, **1** is soluble in organic solvents including nonpolar solvents like benzene and cyclohexane, and **1** is stable to be isolable by sublimation at *ca.* 170° under a reduced nitrogen pressure. Very interestingly, **1** proves to be a powerful metalation reagent. Thus, **1** reacts with hydrocarbons with an acidic hydrogen to produce smoothly the corresponding organocopper compounds.

The equimolar reaction of anhydrous CuCl with *tert*-BuOLi in tetrahydrofuran at an ambient temperature under nitrogen gave a yellow solution containing a pale yellow precipitate. On sublimation of the residue at *ca.* 170° (1 mm) after the removal of tetrahydrofuran, a pale yellow sublimate was obtained in a yield of 80%, which was identified as **1** by the following analyses. The copper content of the sublimate was found by iodometry to be 45.9% (calcd for **1**, 46.5%); the ir spectrum (Nujol) showed absorptions due to the skeletal vibration of the *tert*-butyl group at 1240 and 1180 cm^{-1} and absorptions of *tert*-butyl–O stretching at 940 and 920 cm^{-1} (doublet). The nmr spectrum in benzene showed only one sharp singlet at τ 8.74. The chemical shift of the *tert*-butyl protons was quite similar to that of *tert*-butyl alcohol. The diamagnetism of **1** was confirmed by the absence of esr signal. The *tert*-butoxy group content in **1** was 99%, determined from *tert*-butyl alcohol liberation by an instantaneous acidolysis with acetic acid which gave rise to cuprous acetate quantitatively.

Treatment of **1** with di-*tert*-butyl peroxide gave cupric di-*tert*-butoxide (**2**). The reaction of **1** with an excess of di-*tert*-butyl peroxide in benzene gave a dark green precipitate at 90°. After filtration, washing with benzene, and drying at a reduced pressure, **2** was obtained quantitatively as a yellow green solid. The copper content by iodometry was 30.5% (calcd 30.3%). The ir absorptions of 1240, 1180 and 915, 905 cm^{-1} were compatible with **2**. The methanolysis of **2** gave *tert*-butyl alcohol quantitatively with concomitant formation of cupric dimethoxide.

The thermal stability of **1** was higher than that of **2**. Heating of **2** at about 150° under a reduced nitrogen pressure caused the decomposition and gave a sublimate of **1**. The ir spectrum of the sublimate was identical with that of **1** prepared from CuCl and *tert*-BuOLi. This finding has offered an alternative way of preparation of **1** from CuCl$_2$ and *tert*-BuOLi; *i.e.*, the sublimation of the reaction mixture of anhydrous CuCl$_2$ with *tert*-BuOLi after the removal of the solvent of tetrahydrofuran gave a sublimate of **1** in a yield of 45%. This unusual high thermal stability of **1** may be ascribed to the absence of the β-hydrogen atom to copper, taking into account the decomposition products of thermally unstable cuprous methoxide described previously.[1]

In the metalation reaction using copper salts, copper alkoxide must be a useful reagent because of having a basic alkoxide group to abstract effectively an active hydrogen atom and liberate an alcohol. Thus, there is no need using a basic or buffered condition[2] to avoid inhibition of the reaction by developing acidity. The reaction of **1** with a large excess of phenylacetylene without any additive at room temperature produced immediately a bright yellow solid of cuprous phenylacetylide. The accompanying liberation of *tert*-butyl alcohol was analyzed by glpc and was shown to be almost quantitative.

$$\underset{80\ \text{mmol}}{\text{PhC}{\equiv}\text{CH}} + \underset{4.0\ \text{mmol}}{\textit{tert}\text{-BuOCu}} \longrightarrow \underset{97\%}{\text{PhC}{\equiv}\text{CCu}} + \underset{97\%}{\textit{tert}\text{-BuOH}}$$

The metalation of phenylacetylene by **2** proceeded slowly at room temperature. The analysis of products has led to the following equation

$$\underset{102\ \text{mmol}}{4\text{PhC}{\equiv}\text{CH}} + \underset{2.55\ \text{mmol}}{2(\textit{tert}\text{-BuO})_2\text{Cu}} \longrightarrow \underset{96\%}{2\text{PhC}{\equiv}\text{CCu}} + \underset{82\%}{\text{PhC}{\equiv}\text{CC}{\equiv}\text{CPh}} + \underset{96\%}{4\textit{tert}\text{-BuOH}}$$

where the yield of diphenyldiacetylene was based on the isolated amount by recrystallization from aqueous ethanol.

Cyclopentadiene also reacted readily with **1**. Mixing of **1** with cyclopentadiene at 0° produced in several minutes metallic copper (yield 99%, purity 96%) and *tert*-butyl alcohol (yield 98%). Cyclopentadienylcopper was assumed as the essential intermediate, which was actually isolated as a phosphine complex when the reaction of cyclopentadiene with **1** was carried out in the presence of triethylphosphine. The addition of cyclopentadiene to a petroleum ether solution of **1** and triethylphosphine at −70° gave immediately a white precipitate of $h^5\text{-C}_5\text{H}_5\text{CuPEt}_3$.[3] The reaction temperature of −70° is taken as being indicative of the remarkable metalation reactivity of **1**, which becomes

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[1] G. Costa, A. Camus, and N. Marsich, *J. Inorg. Nucl. Chem.*, 27, 281 (1965).

[2] G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959).

[3] G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, 2, 32 (1956).

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

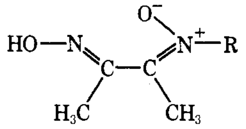
$$\mathbf{3} + H_2O \longrightarrow Co(DH)_2(H_2O)_2^+ + R\cdot \quad (4)$$

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

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).

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

$$Co^{2+} + DH_2 +$$



4

(6)

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 $R = p$-$CH_3C_6H_4CH_2$ and p-$CH_3OC_6H_4CH_2$ ($k = 2 \times 10^5$ and 3×10^5 M^{-1} sec $^{-1}$, respectively.[9] For $R = C_6H_5CH_2$ and p-$FC_6H_4CH_2$, 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).