

It is apparent that KH is far more reactive toward hindered boron compounds than NaH or LiH. Reaction with KH provides a new route of unprecedented ease to highly hindered complex borohydrides; these reagents are of interest as specific reducing agents^{9a} in synthesis and as tools for examining the effect of "B-strain" upon hydride transfer and reduction reactions. The materials also have potential for reduction of transition metal systems.^{9b}

We are currently continuing investigations on reactions of KH and other saline hydrides with weak Brønsted and Lewis acids.

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(9) (a) Potassium triisopropoxyborohydride appears to have unique properties as a reducing agent; it is currently under study. (b) Research in progress.

Charles Allan Brown

Baker Chemistry Laboratory, Cornell University
Ithaca, New York 14850

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Preparation of Ruthenium(0) and Osmium(0) Cyclooctatetraene Complexes

Sir:

Zerovalent complexes of metals in the iron triad continue to attract attention as potential catalysts,¹ as means of studying electrophilic and/or nucleophilic attack on coordinated organic molecules,² as models for "oxidative addition" reactions,³ and, most recently, as desirable analogs to the known ML₅ complexes of d⁸ configuration (*e.g.*, M = Rh(I), L = P(OMe)₃) found to be stereochemically rigid on the nmr time scale at low temperatures.⁴ In general, however, synthetic routes to such species, particularly those not containing carbon monoxide,^{5,6} have been severely limited. We wish to report here the preparation of some Ru(0) and Os(0) cyclooctatetraene complexes employing the dianion of cyclooctatetraene ([COT]²⁻) as an efficient two-electron reducing agent. Preliminary studies show that the method may be used to prepare zerovalent complexes containing group Va ligands and that the Ru(0) cyclooctatetraene complexes will find application as catalysts and as preparative intermediates. This communication is concerned primarily with a description of the preparative method.⁷

Addition of a tetrahydrofuran solution of [K⁺]₂[COT]²⁻ to a stirred suspension of [Ru(NBD)Cl₂]_x

(1) See, for example, A. Carbonaro, A. Greco, and G. Dall'asta, *J. Organometal. Chem.*, **20**, 177 (1969).

(2) See, for example, D. A. White, *Organometal. Chem. Rev., Sect. A*, **3**, 497 (1968).

(3) See, for example, J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **87**, 4008 (1965); **88**, 3504 (1966).

(4) J. P. Jesson and P. Meakin, *J. Amer. Chem. Soc.*, **95**, 1344 (1973).

(5) The most successful method to date has been the isopropyl Grignard method developed by Fischer.⁶ The application of this method toward preparation of complexes containing group Va ligands or the utility of the successfully synthesized complexes as preparative intermediates has yet to be demonstrated.

(6) J. Müller and E. O. Fischer, *J. Organometal. Chem.*, **5**, 275 (1966).

(7) All complexes reported in this communication have been fully characterized by elemental analyses and spectroscopic methods.

(NBD = bicyclo[2.2.1]hepta-2,5-diene) in THF yields a brown reaction mixture. Evaporation to dryness and extraction with pentane followed by chromatography on basic alumina (8% water, pentane eluent) yield (*inter alia*) orange plates of Ru(NBD)(COT) (**1**) in 20–30% yield by low-temperature crystallization. The infrared spectrum of **1** (Nujol) contains a band at 1670 cm⁻¹ which is consistent with COT bonded as a tridentate ligand⁸ while its temperature-dependent spectrum⁹ is consistent with a five-coordinate ground-state geometry containing a plane of symmetry which bisects NBD (through the C=C bonds) and the tridentate COT ligand. The mass spectrum shows a parent peak at *m/e* 298.028 (calcd 298.029); significant loss of H₂ (*x* = 1 or 2) from the parent ion is clearly indicated. The complex is very air sensitive in solution and mildly so in the solid state. Although it cannot be sublimed without decomposition, it may be stored indefinitely at -30° under nitrogen.

Three other products have been isolated in lower yields. Two are found in addition to **1** under the above conditions, yellow Ru(NBD)(C₈H₁₀) (**2**, C₈H₁₀ = 1,3,5-cyclooctatriene, 4% yield) and an intensely colored wine red dimeric species (**3**) whose precise composition is still uncertain.¹⁰ Hydrogenation (or dehydrogenation) of unsaturated hydrocarbon ligands during preparation of complexes analogous to **1** has been observed by Fischer,⁶ and formation of **2** is therefore not unexpected. Complex **3** is probably related to another dimeric species, Ru₂(NBD)₂(COT) (**4**), produced in low yield along with **2** and **3** upon stirring [Ru(NBD)Cl₂]₂, potassium metal, and cyclooctatetraene in THF. The nmr spectrum of **4**¹¹ is consistent with a structure in which COT bridges two metal-metal bonded Ru(NBD) moieties *via* 1,3-coordination to each.

The analogous reaction of [Ru(COD)Cl₂]_x (COD = 1,5-cyclooctadiene) with [K⁺]₂[COT]²⁻ gave yellow crystals of Ru(COD)(C₈H₁₀)¹² and a yellow solid formulated as RuC₁₆H₂₀, both in 10% yield. A broad complicated nmr spectrum suggests that the latter is not solely Ru(COD)(COT); it is considered likely that COD has largely isomerized to what is formally a Ru(II) complex by formation of a π-allyl- and a σ-carbon-metal bond in a manner similar to that observed for Ru(COD)(CO)₃.¹³ A trace (*ca.* 1%) of an orange species was isolated whose mass spectrum indicated it

(8) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3444 (1966).

(9) The limiting spectrum was obtained at -25° in toluene-*d*₈ at 100 MHz: τ 4.64 (2, dd, *J* ≈ 2 and 4 Hz, COT), 5.04 (4, m, COT), 5.86 (2, dd, *J* ≈ 2 and 8 Hz, COT), 6.88 (2, m, NBD methines), 7.28 (4, t, *J* ≈ 2, NBD olefins), 9.00 (2, t, *J* ≈ 1 Hz, NBD methylenes).

(10) The mass spectrum of **3** shows an apparent parent ion at *m/e* 490 although ready loss of H₂ from a species with *m/e* 492 cannot be ruled out at this time. The nmr spectrum of **3** in C₆D₆ at 220 MHz is exceedingly complicated, indicating the structure to be one of low symmetry.

(11) The nmr spectrum of **4** was recorded at 220 MHz in C₆D₆. Assignments were made with the aid of decoupling experiments. The COT resonances occur (in τ units) at -1.69 (2, dd, *J* = 1, 7 Hz), 2.84 (2, dd, *J* = 5, 7 Hz), 4.93 (2, ddd, *J* = 1, 5, 6.5 Hz), and 8.32 (2, d, *J* = 6.5 Hz). The NBD resonances occur at 6.48 (2, br s, NBD-CH), 6.80 (2, t, *J* = 3.5–4.0 Hz, NBD olefin), 6.92 (4, m, NBD olefin), 7.02 (2, br t, *J* = 3.5–4.0 Hz, NBD olefin), 7.58 (2, br s, NBD-CH), and 8.97 (4, br s, NBD-CH₂). The τ 8.97 peak is resolved into two broadened singlets (Δν = 4 Hz) in CDCl₃ (Δν = 1–2 Hz at 100 MHz in CDCl₃). A mirror plane of symmetry passing between the Ru nuclei is favored over a C₂ axis of symmetry.

(12) E. O. Fischer and J. Müller, *Chem. Ber.*, **96**, 3217 (1963).

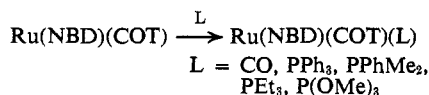
(13) A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organometal. Chem.*, in press.

to be $\text{Ru}_2\text{C}_{24}\text{H}_{32}$ (exact mass 524.059). The complex nmr spectrum of this species suggests that it is not the simple analog of **4**, $\text{Ru}_2(\text{COD})_2(\text{COT})$.

Cyclooctatetraene complexes of Os(0) were prepared similarly from $[\text{Os}(\text{COD})\text{Cl}_2]_x$. In contrast to the Ru case, spectroscopically pure $\text{Os}(\text{COD})(\text{COT})$ was isolated in ca. 25% yield. The known complex, $\text{Os}(\text{COD})(\text{C}_8\text{H}_{10})$,¹² was isolated in 1–2% yield.

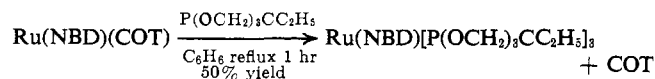
The method of reduction by $[\text{COT}]^{2-}$ can be extended to the preparation of Ru(0) complexes containing phosphine ligands, *i.e.*, $\text{Ru}(\text{PPh}_3)_2(\text{COT})$ and $\text{Ru}(\text{PPhMe}_2)_3(\text{COT})$. The former was isolated as yellow crystals in 50% yield by the reaction of $[\text{K}^+]_2[\text{COT}]^{2-}$ with $\text{RuCl}_2(\text{PPh}_3)_4$ and the latter as orange crystals in 20% yield from $[\text{Ru}_2\text{Cl}_3(\text{PPhMe}_2)_6]^+\text{Cl}^-$. Presumably steric considerations prevent isolation of $\text{Ru}(\text{PPh}_3)_3(\text{COT})$.

$\text{Ru}(\text{PPh}_3)_2(\text{COT})$, $\text{Ru}(\text{NBD})(\text{COT})$, and $\text{Os}(\text{COD})(\text{COT})$ are the first complexes of these metals containing tridentate cyclooctatetraene. (The temperature-dependent nmr spectra of the latter two are analogous to that for $\text{Mo}(\text{COT})(\text{CO})_3$.⁸) It appears, however, that tridentate bonding is tenuous since Ru(0) species¹⁴ containing bidentate COT¹⁵ are formed in seconds at room temperature in the presence of phosphorus ligands or carbon monoxide, *viz.*



Interestingly, there is evidence which suggests that the tendency for COT to prefer bidentate coordination may also play an active role in determining catalytic activity (at least under mild conditions) by allowing the reagents involved to gain access to the metal center. For example, (1) $\text{Ru}(\text{NBD})(\text{COT})$ and $\text{Ru}(\text{PPh}_3)_2(\text{COT})$ are active catalysts (or catalyst precursors) for the hydrogenation of 1-butene under mild conditions (1–2 atm of H₂, 25–60°) while $\text{Ru}(\text{NBD})(\text{COT})(\text{PPhMe}_2)$ and $\text{Ru}(\text{PPhMe}_2)_3(\text{COT})$ are essentially inactive under similar conditions and (2) ethylene reacts irreversibly with $\text{Ru}(\text{NBD})(\text{COT})$ in C₆D₆ to yield species other than the simple adduct, $\text{Ru}(\text{NBD})(\text{COT})(\text{C}_2\text{H}_4)$, as judged by nmr examination of the resultant solution. The above observations should be compared with the extensive investigation of the catalytic activity of $\text{Fe}(\text{COT})_2$ ¹ where similar arguments could be invoked.

Preliminary studies suggest that bidentate COT is reasonably labile and that Ru(0)–COT complexes may therefore serve as preparative materials, *viz.*



Analogous reactions with phosphines (L, *e.g.*, PPhMe_2) suggest (by nmr) that more complicated mixtures containing (*inter alia*) $\text{Ru}(\text{NBD})\text{L}_3$ and $\text{RuL}_x(\text{COT})$ ($x = 2$ or 3) are produced. The scope of this method for preparation of a variety of Ru(0) complexes containing

(14) Corresponding studies of $\text{Os}(\text{COD})(\text{COT})$ behavior have not yet been completed.

(15) In monomeric complexes of metals in the iron triad bidentate COT is bonded through a conjugated double bond system. There is no evidence to suggest deviation from this behavior.

group Va ligands is presently under active investigation.¹⁶

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(16) It should be noted in this context that the rearrangement of hydrocarbon ligands containing methylenic protons (such as 1,5-cyclooctadiene¹⁹) in complexes similar to **1**^{6,12} may preclude their preparative utility in reactions of this type.

(17) Address correspondence this author at Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. 19898.

Richard R. Schrock,*¹⁷ J. Lewis

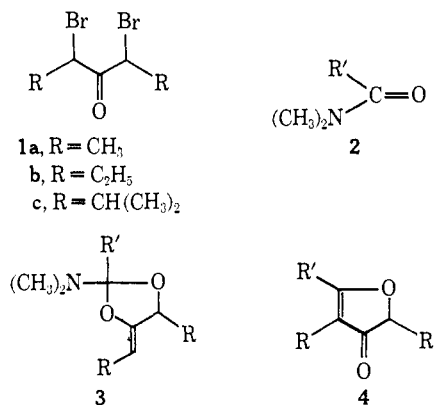
University Chemical Laboratory, Cambridge University
Cambridge, England

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Iron Carbonyl Promoted Reaction of α, α' -Dibromo Ketones and Carboxamides. A Convenient Route to Muscarines *via* Furanones¹

Sir:

Recently Hoffmann and coworkers reported a two-step synthesis of 3(2*H*)-furanones (**4**) which consists of reduction of α, α' -dibromo ketones (**1**) with Zn–Cu couple in the presence of carboxamides **2**, producing the dioxolane derivatives **3**, followed by acid treatment.² The method provides a new route to five-membered heterocycles and can be viewed formally as the construction of a carbon–oxygen bridge between the α and α' positions of the parent dialkyl ketones. This communication describes a related method and its applicability to the synthesis of naturally occurring products.



The modification involves the adoption of $\text{Fe}_2(\text{CO})_9$ as a reducing agent in place of Zn–Cu couple. When a mixture of the dibromo ketone **1b** (8.5 mmol) and $\text{Fe}_2(\text{CO})_9$ (12 mmol) in dry *N,N*-dimethylformamide (DMF) (35 ml) was stirred at 25° for 12 hr under nitrogen, the desired cyclic adduct **4** (R = C₂H₅ and R' = H) was obtained in 64% yield after the usual

(1) Carbon–Carbon Bond Formations Promoted by Transition Metal Carbonyls. VIII. This work was presented in part at the 5th International Conference on Organometallic Chemistry, Moscow, Aug 16–21, 1971, Abstract No. 25. Part VII of this series: R. Noyori, K. Yokoyama, and Y. Hayakawa, *J. Amer. Chem. Soc.*, **95**, 2722 (1973).

(2) H. M. R. Hoffmann, K. E. Clemens, E. A. Schmidt, and R. H. Smithers, *ibid.*, **94**, 3201 (1972); B. K. Carpenter, K. E. Clemens, E. A. Schmidt, and H. M. R. Hoffmann, *ibid.*, **94**, 6213 (1972); M.-A. Barrow, A. C. Richards, R. H. Smithers, and H. M. R. Hoffmann, *Tetrahedron Lett.*, 3101 (1972).