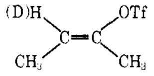
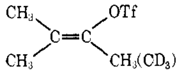
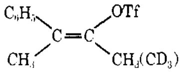
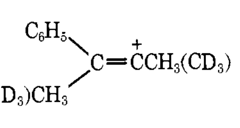
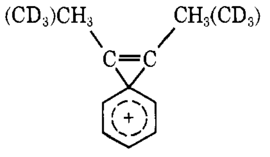
Table II. Summary of β-Deuterium Kinetic Isotope Effects in Vinyl Cations

Substrate	Reactn condn	k_H/k_D	$\Delta\Delta F^{\ddagger a}$	Ref
	60% EtOH, 75°	1.23	143	4b
	60% EtOH, 75°	1.46	87	This work
	60% EtOH, 100°	1.47	95	This work

[a] Average reduction in free energy of activation per deuterium in calories/mole.



5a



5b

usually of considerably smaller magnitude than observed for vinyl cations in this study. Presumably the π system in a vinyl cation transmits the electronic effects more efficiently than a saturated C–C bond in a normal carbonium ion. Hence, such an inverse γ-isotope effect is once again consistent with ionization to an open vinyl cation **5a** for the cis isomer **2**. On the other hand, in the trans isomer **3** the γ-deuterium isotope effect, although small, is positive indicating some charge delocalization into the β carbon in the transition state leading to the intermediate bridged ion **5b**. The fact that the β- and γ-isotope effects in **3** are not equal indicates that the transition state leading to the intermediate ion **5b** occurs early in the reaction coordinate diagram and must be unsymmetrical. In that case the experimentally observed k_H/k_D of 1.04 for **3c** must be a combination of a β and γ effect operating in opposite directions.[4a] Assuming that the γ effect in **3c** would be the same as the observed γ effect of 0.90 in **2c**, one can calculate[4a] a β-secondary isotope effect of 1.15 (1.04/0.90) for **3c** which is within experimental error identical with the observed β effect of 1.16 for **3b**. The unequal isotope effects and the postulated unsymmetrical transition state in the vinylidene phenonium ion are consistent with similar observations in the analogous saturated phenonium ions.[7]

Finally, the available data allow a comparison between secondary kinetic deuterium isotope effects observed in vinyl cations resulting from solvolysis of vinyl substrates of type **1a** and **1b**. The relevant data are shown in Table II. If it is assumed that the *cis*-2-buten-2-yl triflates as well as the 2-methyl-2-buten-2-yl and *cis*-3-phenyl-2-buten-2-yl triflates go to a similar open linear vinyl cation, $RCH_3C{=}C^+CH_3$, then the average reduction in free energy of activation per deuterium ($\Delta\Delta F^{\ddagger}$) is about 50–60% higher for a β-isotopic substitution on the double bond, such as in **1a**, than for β-isotopic substitution on an adjacent saturated β carbon such as **1b**. This observation is in accord with Shiner's hypothesis[8] that the magnitude of β-deuterium isotope effect is strongly dependent upon the dihedral angle between the empty p orbital and the β C–H bond. In the vinyl cation, resulting from **1a**, the β hydrogens on the double bond are rigidly held in the same plane as the empty p orbital allowing for greater hyperconjugative overlap than in the ion resulting from **1b**. Furthermore, overlap is probably better across the shorter C=C double bond in **1a** than across the C—C single bond in **1b**.

Acknowledgment. We thank Mr. R. J. Hargrove for some computer assistance in the calculation of rate data. Financial support by the University of Utah Research Committee, the Research Corporation, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

---

(7) W. H. Saunders, Jr., S. Asperger, and D. H. Edison, *J. Amer. Chem. Soc.*, **80**, 2421 (1958); S. L. Loukas, M. R. Velkou, and G. A. Gregoriou, *Chem. Commun.*, 1199 (1969); S. L. Loukas, F. S. Varveri, M. R. Velkou, and G. A. Gregoriou, *Tetrahedron Lett.*, 1803 (1971).

(8) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Amer. Chem. Soc.*, **85**, 2413 (1963); V. J. Shiner, Jr., and J. S. Humphrey, Jr., *ibid.*, **85**, 2416 (1963); V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, **86**, 945 (1964).

Peter J. Stang,* Thomas E. Dueber
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received May 1, 1972

A Reactive New d^8 Metal Center for Oxidative Addition Reactions

Sir:

Herein we report oxidative addition[1] reactions of Rh(DO)(DOH)pn[2] (**1a**) and its BF_2 derivative **1b**. The structure and reactivity patterns of **1a**,**b** are strikingly similar to those of anionic "supernucleophilic" cobalt(I) and rhodium(I) complexes with dinegative tetradentate ligands.[3] The novel features of **1a**,**b** are the highest reactivity yet reported for an isolated, neutral d^8 complex, the steric constraints afforded by the DOH ligand, and competing chemistry of the oxime bridge.

Coordinatively unsaturated **1a** forms deep blue 1:1 phosphine (Ph_3P, PEt_3) complexes similar to Co(DO)-

---

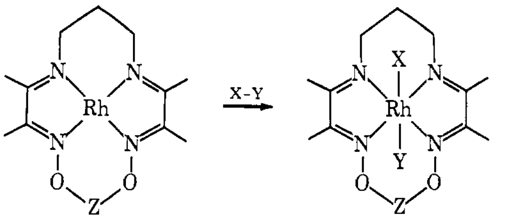
(1) (a) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 54 (1968); (b) J. Halpern, *Accounts Chem. Res.*, 3, 386 (1970).

(2) The synthesis of **1a** is similar to that described for **1b** using basic ethanol as a reducing agent. The molecular structure depicted for **1a** has been confirmed by a complete X-ray crystallographic study. The only surprising feature of this structure is that the intracrystalline arrangement does not afford linear chains of Rh atoms. The closest Rh–Rh distance is 6.7 Å: J. P. Collman, E. B. Fleischer, D. Y. Jester, and D. W. Murphy, unpublished results.

(3) G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, **91**, 3341 (1969).

(DOH)pn(Ph$_3$P) reported by Costa.[4] Three pmr DOH methyl resonances of Rh(DO)(DOH)pn(PEt$_3$) at δ 1.55, 1.80, and 2.30 in the ratio 1:1:2 in the spectrum suggest distortion of the DOH ligand from coplanarity. Surprisingly CO fails to coordinate with **1a**, presumably because the d$_{xz}$ and d$_{yz}$ orbitals are occupied in back-bonding with the (DOH) ligand. We know of no other case of an unsaturated d^8 complex which adds phosphines but not CO.

Treating THF suspensions of **1a** with addenda X–Y affords high yields of the trans rhodium(III) adducts **2a** (eq 1). Adducts have been obtained and characterized using the well known addenda iodine, bromine, acetyl chloride, benzoyl chloride, methyl iodide, ethyl iodide, benzyl chloride, cyclohexyl bromide, triphenyltin chloride, and 6-bromohexene, as well as neopentyl bromide, chloroform, and dichloromethane which seldom form oxidative adducts. The cobalt analogs of some of these complexes have been prepared by other routes by Costa[4] and coworkers. The relative rates of alkyl halide additions—simple primary halides reacting very rapidly but cyclohexyl and neopentyl bromides requiring several hours at reflux—are suggestive of two electron changes (nucleophilic attack at carbon). Further support for this hypothesis is provided by the absence of by-products or rearrangement in the addition of 6-bromohexene since the 6-hexenyl radical closes irreversibly and rapidly (k_1 = 10^5 sec^{-1})[5] to a five-membered ring. A final decision on this point must await the results of kinetic and stereochemical studies in progress. It may be that either a one or two electron path will dominate depending on the nature of the alkylating agent or reaction conditions as observed for (Me$_3$P)$_2$Ir(CO)Cl.[6,7] A one electron path (radical) is likely for the reactions of **1a** with CCl$_4$ and trimethyltin chloride, both of which yield **2a** (X = Y = Cl).



(1)

1a, Z = H
1b, Z = BF$_2$

2a, Z = H,
b, Z = BF$_2$
c, Z = SnCl$_3$

All of the adducts **2** described above exhibit the trans stereochemistry anticipated in view of the tendency for the tetradentate ligand to remain coplanar. This assignment is based on pmr spectra showing two distinct ligand methyl singlets (6 H each) near δ 2.25 on or near a multiplet (2 H) due to the central bridge CH$_2$, as well as an NCH$_2$ multiplet near δ 4.0 (4 H) and an O–H$\cdots$O resonance near δ 11.0 to 13.0. The α-CH groups are shifted upfield (CH$_3$ = 0.20, CH$_2$Cl = 3.38, CHCl$_2$ = 5.85, and (CH$_3$)$_3$CCH$_2$ = 1.00) and split by ^{103}Rh ($J_{\text{Rh-H}}$ = 1.2 Hz). The structure assigned to the 6-hexenyl adduct is based on pmr data showing a terminal olefin (δ 4.70 (m, 1-H), 4.90 (m, 1-H), and 5.5 (m 1-H)).

Certain molecules have a marked tendency to form cis adducts with d^8 centers.[1] At first it seemed that the steric constraint of the DOH ligand might preclude cis addition. For example H$_2$, simple olefins and acetylenes gave no indication of adduct formation although H$_2$ under forcing conditions (100°, 100 psi) decomposed **1a** to form a Rh mirror. However, activated olefins and acetylenes (TCNE, dimethyl furmarate, and dimethyl acetylenedicarboxylate) do form stable 1:1 adducts. The tetradentate ligand is distorted from planarity as indicated by four DOH methyl signals (δ 1.60, 1.70, 1.90, and 2.15) and two ester methyl signals (δ 3.35 and 3.45) in the pmr spectrum of the dimethylacetylene adduct.

The oxime O–H$\cdots$O bridge in **1a** reacts with protonic and Lewis acids complicating their oxidative addition reactions. One equivalent of HCl afforded a simple adduct **2a** (X = H; Y = Cl; $\nu_{\text{Rh-H}}$ 2065 cm^{-1}) with a closed oxime bridge (ν_{OH} 2400 cm^{-1}) whereas excess HCl yielded a hydride ($\nu_{\text{Rh-H}}$ 2030 cm^{-1}) with a ruptured oxime bridge[8] (ν_{OH} 3400 cm^{-1}) bond. Both adducts spontaneously decompose over a few hours in the solid state. The latter complex afforded the dichloride **2a** (X = Y = Cl), and the simple adduct (X = H, Y = Cl) gave an uncharacterized species with an open oxime bridge. Stannic chloride gave an adduct analyzing for Rh(DO)(DOH)pnSn$_2$Cl$_7$ thought to have structure **2c** (X = SnCl$_3$, Y = Cl).

In order to rule out the participation of the oxime bridge in reactions of **1a**, the corresponding BF$_2$ adduct was prepared by stirring **2a** (X = Y = Cl) with BF$_3$·O(C$_2$H$_5$)$_2$[9] and reducing to the rhodium(I) complex **1b**, which underwent rapid oxidative addition reactions as before. The BF$_2$ adducts are less soluble and more soluble alkyls were needed to obtain satisfactory pmr spectra. For example, the amyl iodide adduct **2b** (X = n-C$_5$H$_{11}$, Y = I) was prepared and characterized by pmr and elemental analyses. Apparently the BF$_2$ bridge does not introduce enough additional rigidity into the ligand to prevent cis additions. A 2:1 adduct whose spectral properties are consistent with a metallocyclopentadiene[10] structure was formed from CH$_3$O$_2$CCCCO$_2$CH$_3$ and **2b**. Again the presence of four DOH methyl signals (δ 1.75, 1.85, 2.00, and 2.25) are indicative of deviation from coplanarity. The change in stoichiometry of the acetylene adducts of **1a** and **1b** is puzzling. Strong Lewis acids add to **1b** without interference by the bridge. Thus SnCl$_4$ gave **2b** (X = SnCl$_3$, Y = Cl). A more interesting example is the addition of π-C$_5$H$_5$Fe(CO)$_2$SnCl$_3$ to **1b** forming an adduct thought to have the structure **2b** (X = π-C$_5$H$_5$-Fe(CO)$_2$SnCl$_2$, Y = Cl) although the alternative structure (X = SnCl$_3$, Y = π-C$_5$H$_5$Fe(CO)$_2$) cannot be ruled out by available spectral data. Treatment of this adduct with Cl$_2$ gave **2b** (X = SnCl$_3$, Y = Cl) consistent with either structure. A novel aspect of this adduct is the presence of ten different elements of which seven were analyzed.

---

(4) G. Costa, G. Mestroni, and E. De Savorgnani, *Inorg. Chim. Acta*, 3, 323 (1969).

(5) D. J. Carlsson and K. V. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

(6) F. R. Jensen and B. Knickel, *J. Amer. Chem. Soc.*, **93**, 6339 (1971).

(7) J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, **94**, 4043 (1972).

(8) R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 1951 (1965). These weak, broad O–H bands are difficult to distinguish and are not especially reliable for structural characterization.

(9) G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962).

(10) J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, 7, 1298 (1968).

The similarity in structure and patterns of reactivity of the neutral Rh(DO)(DOH)pn and the anionic "supernucleophiles" of Co(I) and Rh(I) make one wonder if the mechanistic pathways are not similar, and if so do those pathways extend to other metal centers.

Acknowledgments. This work has been supported by ARPA Contract No. N00014-67-A-0112-0056, National Science Foundation Grant No. GP20273X, and NATO Grant No. 5-2-05B 504 632.

James P. Collman,* Donald W. Murphy, Giuliano Dolcetti
Department of Chemistry, Stanford University
Stanford, California 94305

Received November 27, 1972

Synthesis of Hemifluorinated Ketones Using Disodium Tetracarbonylferrate(−II)

Sir:

Although hemifluorinated ketones, RCOR′, where R is a simple alkyl or aryl and R′ is a perfluorinated alkyl or aryl, can be prepared by several methods,[1-12] none of these procedures lend themselves to the preparation of such ketones in which R bears a functional group. We wish to report simple, single-flask syntheses of these hemifluorinated ketones using $Na_2Fe(CO)_4$, an inexpensive transition metal reagent. These methods give good to excellent yields and can be employed in cases in which the hydrocarbon group R possesses unmasked nitrile, ester, or chloro groups.[13]

Earlier we employed $Na_2Fe(CO)_4$ to prepare unsymmetrical ketones[15,16] by sequentially adding two different aliphatic halides or sulfonates (eq 1 and 2). These *in situ* ketone syntheses were shown to go through either acyl or alkyl iron(0) intermediates **1** or **2** which have been isolated as their $[(Ph_3P)_2N^+]$ salts.[18] Our attempts to extend the procedures shown in eq 1 and 2 to the preparation of hemifluorinated ketones using perfluoroalkyl halides failed to give appreciable yields (Table I, a). This failure is probably caused by the reversed polarities of perfluoroalkyl halides,[19] $R_f^{\delta-}{-}X^{\delta+}$. Metal carbonyl anions have been reported to react with perfluoroalkyl iodides apparently through attack at iodine affording products of the type shown in eq 5.[20-23]

On the other hand, we have successfully used perfluoro acid chlorides, anhydrides, and pentafluorophenyl iodide to prepare these hemifluorinated ketones (Table I). For example, the method shown in eq 1 may be used by first introducing the perfluoroacyl group with the corresponding acid chloride and then adding an alkylating agent (Table I, g). However, this procedure is limited to very reactive alkylating reagents such as benzyl halides in the second step. Pentafluorophenyl iodide as the second reagent (R′X) gives good yields in the method shown in eq 1 (example b) but poor yields by that of eq 2 (d). Nonfluorinated aromatic iodides afford very low yields by method 1.

Earlier we found the methods outlined in eq 3 and 4 to give very low yields of ketones when ordinary aliphatic acid chlorides or anhydrides are employed as the second reagent.[24] However, perfluoroacyl chlorides (and anhydrides) afford good to excellent yields of hemifluorinated ketones by these methods (Table I). These procedures have all of the versatility of our earlier methods for the *in situ* generation of acyl and alkyl iron intermediates (**1** and **2**), starting from aliphatic halides and tosylates or acid chlorides and making use of the dramatic solvent effects manifested by these reactions.[25] Furthermore, unmasked functionality can be present in the nonfluorinated group R as illustrated by examples e, k, l, m, and o.

All of the compounds listed in Table I have been isolated and characterized by elemental analyses, pmr, and ir. We have demonstrated that the ketone in example h is formed *in situ* at 25° and not in the work-up by removing the product, $n\text{-}C_8H_{17}COC_3F_7$, from the mixture at reduced pressure. A typical procedure (m) is illustrated by synthesis of $n\text{-}C_7F_{15}COC_6H_{12}CN$ using eq 3. Into a slurry of $Na_2Fe(CO)_4$ (867 mg, 4.0 mmol) in 25 ml of THF at 25° under N_2 was injected $Br(CH_2)_6CN$ (0.56 ml, 3.6 mmol). The flask was flushed with CO and stirred under 5 psi for 5 hr, after which $n\text{-}C_7F_{15}COCl$ (1.14 ml, 4.60 mmol) was injected. The mixture was stirred for 8 hr and then treated with acidified brine and extracted twice with ether. The organic layer was dried and concentrated to an oil which was chromatographed on silica with hexane. Removal of hexane and bulb-to-bulb distillation afforded 1.32 g (72%) of $n\text{-}C_7F_{15}COCH_2(CH_2)_4CH_2CN$ as a colorless liquid.

The different course that these reactions take with perfluoroacyl and pentafluorophenyl halides compared with hydrocarbon analogs (reactions 3 and 4 affording high yields with the former and low yields with the latter) is not understood. However, these

---

(1) J. H. Simons, W. T. Black, and R. F. Clark, *J. Amer. Chem. Soc.*, **75**, 5621 (1953).

(2) K. T. Dishart and R. Levine, *ibid.*, **78**, 2268 (1956).

(3) R. Fuchs and G. J. Park, *J. Org. Chem.*, 22, 993 (1957).

(4) E. T. McBee, O. R. Pierce, and D. D. Meyer, *J. Amer. Chem. Soc.*, 77, 917 (1955).

(5) A. Sykes, J. C. Tatlow, and C. R. Thomas, *J. Chem. Soc.*, 835 (1956).

(6) D. S. Breslow, H. G. Walker, R. S. Yost, J. C. Shivers, and C. R. Hauser, *J. Amer. Chem. Soc.*, **68**, 100 (1946).

(7) L. B. Barkley and R. Levine, *ibid.*, **75**, 2059 (1953).

(8) W. R. Nes and A. Burger, *ibid.*, 72, 5409 (1950).

(9) H. F. Bluhm, H. V. Down, and H. D. Zook, *ibid.*, 77, 4406 (1955).

(10) D. A. Rausch, A. M. Lovelace, and L. E. Coleman, *J. Org. Chem.*, 21, 1328 (1956).

(11) T. F. McGrath and R. Levine, *J. Amer. Chem. Soc.*, 77, 3656 (1955).

(12) N. N. Vorozhtsov, V. A. Barkhash, N. G. Ivanova, S. A. Anichkina, and O. I. Andreevskaya, *Dokl. Akad. Nauk SSSR*, **159**, 125 (1964); *Chem. Abstr.*, **62**, 4045a (1965).

(13) Based on our experience using $Na_2Fe(CO)_4$ to prepare carboxylic acid derivatives,[14] ketones are also not usually attacked by this reagent.

(14) J. P. Collman, S. R. Winter, and R. G. Komoto, *J. Amer. Chem. Soc.*, **95**, 249 (1973).

(15) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972).

(16) Tsutsumi and coworkers[17] obtained moderate yields of unsymmetrical ketones by treating lithium acylferrates with acid chlorides and benzyl halides.

(17) (a) I. Rhee, M. Ryang, and S. Tsutsumi, *J. Organometal. Chem.*, **9**, 361 (1967); (b) Y. Sawa, M. Ryang, and S. Tsutsumi, *Tetrahedron Lett.*, 5189 (1960); (c) Y. Sawa, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **35**, 4183 (1970).

(18) W. O. Siegl and J. P. Collman, *J. Amer. Chem. Soc.*, **94**, 2516 (1972).

(19) F. G. A. Stone and P. M. Treichel, *Advan. Organometal. Chem.*, 178 (1964).

(20) W. Hieber and E. Lindner, *Chem. Ber.*, **95**, 273 (1962).

(21) W. Beck, W. Hieber, and H. Tengler, *ibid.*, 94, 862 (1961).

(22) W. Hieber, W. Beck, and E. Lindner, *Z. Naturforsch. B*, **16**, 229 (1961).

(23) J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, **90**, 2282 (1968).

(24) S. R. Winter, N. W. Hoffman, and J. P. Collman, unpublished results.

(25) J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Amer. Chem. Soc.*, 94, 5905 (1972).