positive charges, are electrophilic; also the electrophilic α-carbon atom in $MpCCH_2$ bears considerable negative charge. The same situation was found in carbyne complexes, to which many various nucleophiles add.[5,6]

In the last years, nucleophilic additions to several kinds of organometallic complexes have been recognized as frontier controlled,[5-7,41-46] but no electrophilic additions have been attributed solely to frontier orbitals.[46] This deserves further study.

In view of the preceding discussion, we would be surprised to learn about nucleophilic attack at the α-carbon atoms in the acetylide and vinyl ligands bonded to $CpML_2$ fragments. The LUMO in FpCCH is such that, if a nucleophile adds to that molecule, we would expect it to attack the carbonyl atom. These beliefs of ours perhaps have some support in the behavior of complexes $CpFe(dppe)NCMe^+$[47] because nitrile is similar to acetylide. Various anions, some of them potent nucleophiles, replace the nitrile ligand without any apparent side reactions such as additions. This is not a proof of the hypothesis, but it is consistent with our finding that the LUMO in $Fp'NCH^+$ does not have the properties that would make this complex electrophilic.

Several other ligands in transition-metal complexes undergo α attack by nucleophiles and β attack by electrophiles. Among them are N_2,[48] CS,[49] CSe,[3] CN^-,[3] and NC^-.[3] These regioselective additions are fairly common, and the causes to which we attribute them in this study may be rather general.

Acknowledgment. We are grateful to several colleagues for their comments and information about the chemical reactions we examined. S. G. Harsy and Professor P. M. Treichel, both of this department, read the manuscript and commented upon it. Professors M. I. Bruce of University of Adelaide, K. G. Caulton of Indiana University, A. Davison of Massachusetts Institute of Technology, and R. P. Hughes of Dartmouth College kindly informed us about their experimental work. The research was supported by the National Science Foundation, Grant CHE 7950005. N.M.K. has been a Fulbright Fellow since 1978 and is a Procter and Gamble Fellow for 1981–1982.

Registry No. $CpFe(PH_3)_2^+$, 81616-25-3; $CpFe(CO)_2CCH$, 33029-77-5; $CpFe(PH_3)_2CCH$, 81616-26-4; $CpFe(PH_3)_2NCH^+$, 816616-27-5; $CpMn(CO)_2CCH_2$, 81616-28-6; $CpFe(CO)_2CCH_2^+$, 81616-29-7; $CpFe(PH_3)_2CCH_2^+$, 81616-30-0; $CpFe(PH_3)_2CHCH_2$, 81616-31-1; $CpFe(PH_3)_2CH_2^+$, 81616-32-2.

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(45) Semmelhack, M. F.; Clark, G. R.; Farina, R.; Saeman, M. *J. Am. Chem. Soc.* **1979**, *101*, 217–218.

(46) Albright, T. A.; Carpenter, B. K. *Inorg. Chem.* **1980**, *19*, 3092–3097.

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(49) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73–89.

Hydrido and Hydroxycarbonyl Compounds of the Carbonyl(η-cyclopentadienyl)nitrosylrhenium Group

James R. Sweet and William A. G. Graham*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received December 16, 1981

Reaction of $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2][BF_4]$ (**2**) with $Et_3N\text{-}H_2O$ in acetone at 50 °C affords thermally robust $(\eta\text{-}C_5H_5)Re(NO)(CO)H$ (**1**) in excellent yield as low-melting orange crystals. The stable yellow metallocarboxylic acid $(\eta\text{-}C_5H_5)Re(NO)(CO)COOH$ (**3**) precipitates when base (Et_3N or NaOH) is added to a solution of **2** in water. Although **3** is stable in anhydrous THF, catalytic amounts of strong bases produce **1** rapidly and quantitatively at room temperature, establishing the instability of the carboxylate anion **5** presumed to be formed by deprotonation of **3** under these conditions. The latter anion is more stable in water and is a probable intermediate in the above synthesis of **1**. The high thermal stability of **1** and the more facile loss of CO_2 from the carboxylate **5** than from **3** itself are discussed in terms of the strength of the Re–CO bond. The bromide $(\eta\text{-}C_5H_5)Re(NO)(CO)Br$ is formed in good to excellent yield from **1** and CBr_4, Br_2, or *N*-bromosuccinimide. Hydride abstraction from **1** by $[Ph_3C][PF_6]$ in the presence of donor ligands yields salts $[(\eta\text{-}C_5H_5)Re(NO)(CO)L][PF_6]$ (L = acetonitrile, tetrahydrofuran, acetone).

Introduction

A 1972 communication from this laboratory described the synthesis of the new rhenium hydride $(\eta\text{-}C_5H_5)Re(NO)(CO)H$, **1**.[1,2] Its rather high thermal and oxidative stability were noted, but no reactions were reported. It was only the second example of a nitrosyl hydride, the first having been prepared in 1962 by Hieber and Tengler.[3] Hydride **1** was obtained by reaction of the carbonyl cation **2** with triethylamine and water in acetone (eq 1).[1] The intermediacy of **3** was proposed, but no attempt was made to isolate such a species. We report here details of the preparation of **1** and several of its reactions, which suggest that it will become a useful starting point in synthesis. The results demonstrate a lack of acidity for **1**; its reactions are

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(1) Stewart, R. P.; Okamoto, N.; Graham, W. A. G. *J. Organomet. Chem.* **1972**, *42*, C32.

(2) The prefix η used alone implies that all the atoms in a ring or chain, or all the multiply bonded ligand atoms, are bound to the central atom: International Union of Pure and Applied Chemistry, "Nomenclature of Inorganic Chemistry", 2nd ed. (Definitive Rules 1970); Butterworths: London, 1971. See also: *Pure Appl. Chem.* **1971**, *28*, No. 1.

(3) Hieber, W.; Tengler, H. *Z. Anorg. Allg. Chem.* **1962**, *318*, 136.

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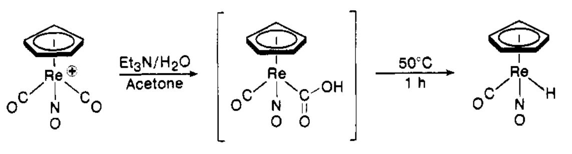

2 3 1 (1)

instead dominated by its ability to act as a hydride donor.

A second matter addressed in this paper is the proposed metallocarboxylic acid of eq 1. Recent work has drawn attention to the ability of the (η-C_5H_5)Re(NO)(CO) moiety to form complexes of uncommonly high stability with organic functional groups. Thus, hydride ion attacks the carbonyl carbon of cation **2** leading to the formyl derivative (η-C_5H_5)Re(NO)(CO)CHO.[4-6] It therefore seemed likely that **3**, the product of hydroxide ion attack on **2**, would be isolable. We have found this to be the case as have Casey et al.,[4] who briefly described the compound during the course of this work.

Metallocarboxylic acids (or hydroxycarbonyls) are usually regarded as key intermediates in water gas shift catalysis,[7] although only a few have been isolated and fully characterized.[8-11] Little detailed information is available on their properties, and in the present context the most interesting of these is the decarboxylation process. Although loss of carbon dioxide from these compounds has been known or assumed to proceed more[12] or less[8] readily, it is only recently that experimental evidence pertinent to the decarboxylation mechanism has become available.

For these reasons, **3** assumes an importance that extends well beyond the question of its intermediacy in eq 1. We report in this paper a number of interesting and perhaps unexpected observations on **3** and its reaction with bases.

Results and Discussion

Preparation of (η-C_5H_5)Re(NO)(CO)H (1). In the original report,[1] (η-C_5H_5)Re(NO)(CO)H (**1**) was synthesized in 60% yield as an orange oil. Optimization of reaction conditions and careful product recovery have now increased the yield to 93%, and the compound has been obtained as orange crystals (mp 30.5–31.0 °C) which are stable in air. The ^{1}H NMR signal of the hydride proton at δ −8.50 is rather broad but sharpens at −70 °C; we attribute the broadening to rapid relaxation by the rhenium quadrupole, and the sharpening to a slowing of this process with increased solvent viscosity at low temperatures. Raman spectra of **1** and its deuterium analogue, (η-C_5H_5)Re(NO)(CO)D (**4**), as neat liquids show ν_{Re-H} and ν_{Re-D} at 2013 and 1445 cm^{-1}, respectively (ratio 1.39); ν_{Re-H} is discernible in the IR of a hexane solution as a broad, weak absorption at 2011 cm^{-1}.

Despite these unexceptional spectroscopic properties for the Re–H bond of **1**, the thermal stability of the compound is remarkable.[1] We now find that **1** undergoes no noticeable decomposition during heating in decane (bath temperature 180 °C) for 1 week provided heterogeneous conditions are avoided (see Experimental Section). The question arises why the compound is so much more stable than other carbonyl hydrides with comparable ν_{M-H}, which ought to be a rough indicator of bond strength. A plausible answer is that the thermal decomposition of a great many metal carbonyl hydrides may proceed by a bimolecular process involving carbon monoxide dissociation, not M–H homolysis, as the pathway. A bimolecular process of this sort was proposed by Norton for osmium alkyls and hydrides[13] and clearly has general implications. The thermal stability of **1** would result, according to this argument, not from an exceptionally strong Re–H bond but from its nonlabile carbonyl group.[14]

Preparation of (η-C_5H_5)Re(NO)(CO)COOH (3). During preparation of **1**, we noted that although addition of Et_3N to yellow water–acetone solutions of [(η-C_5H_5)Re(NO)$(CO)_2$]$^+$ produced an immediate orange coloration, **1** was generated only slowly at room temperature. We suspected that the initial orange color might be due to (η-C_5H_5)Re(NO)(CO)COOH (**3**), which in analogy to (η-C_5H_5)Fe(CO)(PPh_3)COOH[10] (**6**) would be expected to exist in excess base at least partly as the carboxylate anion. In fact, **3** precipitated as analytically pure yellow microcrystals when the reaction of **2** with base (Et_3N or NaOH) was carried out in water; when excess base is added in this reaction, **3** dissolves to form an orange solution, presumably of the carboxylate anion **5** (see below). The pure carboxylic acid **3** is stable in air and is thermally fairly stable (slow decomposition beginning at ca. 90 °C).

Reaction of **3** with HBF_4 etherate in dichloromethane converts it back to the carbonyl cation.[15] Reversible interconversion of **2** and **3** thus proceeds as shown in eq 2,

$$\underset{\mathbf{2}}{[(\eta\text{-}C_5H_5)Re(NO)(CO)_2]^+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\mathbf{3}}{(\eta\text{-}C_5H_5)Re(NO)(CO)COOH} \quad (2)$$

and the behavior of the rhenium system in this reaction resembles that of (η-C_5H_5)Fe(CO)(PPh_3)COOH,[10] $(Et_3P)_2$Pt(Cl)COOH,[11,12] and $(PhMe_2P)_2IrCl_2$(CO)COOH.[8]

As noted in the Introduction, the reaction of OH^- with **2** involves nucleophilic attack on an activated CO ligand. This activation is no doubt provided by the positive charge on carbon that results from coordination, as was the case in borohydride reactions of **2**.[4-6] We note in passing that the phosphine-substituted cations [(η-C_5H_5)Re(NO)(CO)L]$^+$ (L = PPh_3, PMe_2Ph)[16] undergo no reaction with triethylamine–water under similar conditions. This would follow from increased back-donation to the remaining CO and the consequent decrease in the partial positive charge on carbon. A similar rationale would account for the inertness of [(η-C_5H_5)Fe(diphos)CO]$^+$ to attack by OH^- or BH_4^-.[10]

Decarboxylation of (η-C_5H_5)Re(NO)(CO)COOH (3). Once the hydroxycarbonyl **3** had been isolated, its postulated intermediacy[1] in the preparation of **1** could be tested.

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[4] Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741.

[5] Tam, W.; Wong, W. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589.

[6] (a) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811. (b) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173*, C9.

[7] (a) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31. (b) A detailed kinetic study which appeared after submission of this paper is especially relevant: Pearson, R. G.; Mauermann, H. *J. Am. Chem. Soc.* **1982**, *104*, 500.

[8] Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A*, **1969**, 443.

[9] Appleton, T. G.; Bennett, M. A. *J. Organomet. Chem.* **1973**, *55*, C88.

[10] Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627.

[11] Catellani, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566.

[12] (a) Clark, H. C.; Dixon, K. R.; Jacobs, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 1346. (b) Clark, H. C.; Jacobs, W. J. *Inorg. Chem.* **1970**, *9*, 1229.

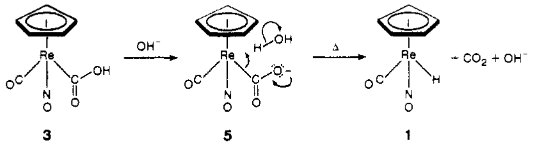
[13] Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139 and references cited.

[14] We thank Professor H. D. Kaesz for discussions of this point.

[15] Conversion of **3** to [(η-C_5H_5)Re(NO)$(CO)_2$]$^+$ by trifluoroacetic acid was mentioned by Casey et al.[4] We have confirmed this, but note in the room temperature reaction the appearance, with time, of infrared bands indicative of (η-C_5H_5)Re(NO)(CO)$(OOCCF_3)$, a compound which we have prepared by another route and fully characterized.

[16] Sweet, J. R.; Graham, W. A. G. In preparation. In the series of cations [(η-C_5H_5)Re(NO)(CO)L]$^+$, ν_{CO} (CH_2Cl_2) is as follows: 2092, 2036 cm^{-1}, L = CO; 2023 cm^{-1}, L = PPh_3; 2022 cm^{-1}, L = PMe_2Ph.

When **3** was subjected to the conditions of the hydride preparation (Et_3N–H_2O, acetone, 50 °C, 1.0 h), it gave **1** as the sole product in >90% yield. However, when **3** was heated for 1.0 h at 50 °C in *anhydrous* acetone (no Et_3N, no H_2O), hydride **1** was not formed. We conclude that under these conditions, CO_2 loss occurs less readily from the carboxylic acid **3** than from a species formed by reaction of **3** with hydroxide ion.[17] Based on the results of Pettit et al. with **6**,[10] we suggest that this species may be the carboxylate anion **5** formed by simple deprotonation of **3**. This process is shown somewhat schematically in eq 3 in such a way as to suggest that the unknown anion $[(\eta\text{-}C_5H_5)Re(NO)(CO)]^-$ need not actually exist as a discrete intermediate. This is a moot point because, if formed, the anion would be strongly basic and rapidly acquire a proton (see later remarks on the lack of acidity of **1**).



(3)

An alternative mechanism for decarboxylation of metallocarboxylic acids under basic conditions invokes nucleophilic attack by hydroxide on the carboxyl carbon, forming an intermediate $MC(OH)_2O^-$ species.[19] Product would then arise by β-hydrogen transfer to the metal and elimination (presumably) of bicarbonate ion.[22] While such a route may not be readily distinguishable from the one shown in eq 3, we note that formation of **1** occurs with vigorous evoultion of CO_2 (see Experimental Section); this observation is not consistent with the elimination of bicarbonate under the basic conditions of the synthesis (eq 1).

To better understand the mechanism of decarboxylation and in an attempt to isolate the carboxylate **5**, we have studied the reaction of **3** with a variety of bases in anhydrous tetrahydrofuran. Acid **3** readily dissolved in THF forming yellow solutions from which it could be recovered unchanged. Heating **3** in dry THF for 1 h at 50 °C resulted in some decomposition, but no detectable **1** was formed. When **3** was treated with 1 mol of $Na[N(SiMe_3)_2]$ in THF at room temperature, very rapid and complete conversion to $(\eta\text{-}C_5H_5)Re(NO)(CO)H$ (**1**) occurred. Identical results were obtained by using 0.6, 0.35, or 0.05 mol of base/mol of **3**. Thus, only catalytic amounts of this strong base are required for the decarboxylation.

The results were the same when **3** in dry THF was treated with lithium 2,2,6,6-tetramethylpiperidide.[23,24] Nucleophilic attack on the carboxyl carbon by either of these highly hindered bases seems unlikely; it is probable in our view that deprotonation forming **5** is the initial step here, followed by rapid CO_2 loss. The catalytic cycle would then be represented by eq 4. The final step (eq 4c) suggests that the unobserved $[(\eta\text{-}C_5H_5)Re(NO)(CO)]^-$ anion is a very strong base and is consistent with the failure of $Na[N(SiMe_3)_2]$ to deprotonate **1** as discussed below.

$$Re\text{–}COOH + NR_2^- \rightarrow Re\text{–}COO^- + HNR_2 \qquad (4a)$$

$$Re\text{–}COO^- \rightarrow Re^- + CO_2 \qquad (4b)$$

$$Re^- + HNR_2 \rightarrow ReH + NR_2^- \qquad (4c)$$

Initially, it appeared that the rapid decarboxylation of **5** observed above would preclude its isolation or direct observation. However, the anion has some stability in water. The acid **3** is slightly soluble in water forming bright yellow solutions from which it is readily extracted with CH_2Cl_2. Addition of hydroxides (LiOH, NaOH, KOH, aqueous Et_4NOH) or Et_3N to suspensions of **3** in water results in rapid dissolution to give orange-yellow solutions from which CH_2Cl_2 extracts neither **3** nor **1** nor any other species. These solutions, believed to contain $[(\eta\text{-}C_5H_5)Re(NO)(CO)COO]^-$ (**5**), are stable at room temperature and when heated produce **1** only slowly. ^1H NMR monitoring during reaction of **3** with NaOH in D_2O showed the $\eta\text{-}C_5H_5$ signal at δ 5.77 due to **3** was replaced with a new signal at δ 5.65 which we assign to **5**. As the solution is acidified by using aqueous HBF_4, the peak due to **3** reappears followed by that of the carbonyl cation **2** δ 6.21 as shown in eq 2. The enhanced stability of the carboxylate anion in water is attributed to hydrogen bonding.

The stabilizing effect of H_2O on the carboxylate anion also influences the acidity of **3**. In water, **3** is a weak acid but is substantially deprotonated by Et_3N[25] (see above). However, **3** is *not* deprotonated by equimolar Et_3N in anhydrous acetone or THF to an extent that can be detected by a change in the IR; a still more sensitive indication of the lack of deprotonation is that no **1** is formed when the anhydrous acetone solution of equimolar **3** and Et_3N is heated at 50 °C for 1 h.

The foregoing observations on **3** are not without relevance as far as catalysis mechanisms for the water gas shift reaction are concerned.[7] They further invite comparison with what has been reported for $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)COOH$ (**6**).[10] The latter is considerably less stable thermally than **3**, since it loses CO_2 rapidly on warming in benzene. On the other hand, the iron carboxylate was isolated as a stable microcrystalline potassium salt, which did not decompose when its solution in dry formamide was heated to 100 °C.[10]

We think that the different thermal stabilities of the carboxylic acids **3** and **6** can be explained in terms of the differing lability of the other ligands in the two cases. We would expect loss of CO_2 from the neutral iron complex **6** to proceed by a β-elimination pathway resembling the one proposed for analogous alkyls:[26] phosphine dissocia-

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[17] This observation has precedent. Exchange of ^{18}O between $H_2{}^{18}O$ and $[Mn(CO)_4(diphos)]^+$ via a presumed neutral hydroxycarbonyl intermediate was catalyzed by Et_3N,[18] which also increased the rate of a competitive reaction in which $HMn(CO)_3(diphos)$ was formed; for the latter reaction, a mechanism involving CO_2 loss from the deprotonated hydroxycarbonyl was favored.[18b] Titration of $(PhMe_2P)_2IrCl_2(CO)COOH$ in acetone–water with NaOH liberates CO_2 and HCl.[8]

[18] (a) Darensbourg, D. J.; Foelich, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5940. (b) Darensbourg, D. J.; Froelich, J. A. *Inorg. Chem.* **1978**, *17*, 3300.

[19] Intermediates of this sort, resembling those established in the addition mechanism of ester hydrolysis,[20] were apparently first suggested in the context of metal carbonyl base reactions by Kruck et al.,[21] although without supporting evidence. They are often mentioned as alternatives to the "simple deprotonation" process (for example, in ref 18a and references cited therein). On the evidence of a kinetic study of the reaction of $[ClPt(CO)(PEt_3)_2]^+$ with H_2O in neutral or acidic aqueous solutions, attack by H_2O on the carboxyl carbon of the intermediate $ClPt(COOH)(PEt_3)_2$ was considered the most likely mechanism, although direct decarboxylation of the neutral hydroxycarbonyl was not ruled out.[12b]

[20] Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; p 440.

[21] (a) Kruck, T.; Noack, M. *Chem. Ber.* **1964**, *97*, 1693. (b) Kruck, T.; Höfler, M.; Noack, M. *Ibid.* **1966**, *99*, 1153.

[22] We acknowledge the suggestion of a reviewer that this pathway deserves consideration.

[23] Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 581, 582.

[24] Several other bases also react with **3** in anhydrous THF to form **1**: $KOCMe_3$, $LiOH\cdot H_2O$, NaOH, KOH, and aqueous Et_4NOH.

[25] The basicity of Et_3N would also be enhanced in an aqueous medium by hydrogen bonding: Huheey, J. E. "Inorganic Chemistry: Principles of Structure and Reactivity", 2nd ed.; Harper and Row: New York, 1978.

[26] Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789.

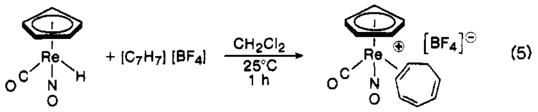
tion would be the first step in the process. We have already remarked on the high barrier to dissociation of CO in connection with the stability of 1. This high barrier would block the conventional β-elimination pathway for 3, and the sequence shown in eq 3 (which does not require ligand dissociation) would have the lower activation energy.

It is more difficult to compare the iron and rhenium carboxylate anions, but the iron anion appears more tractable and stable.[27] Its high stability in dry formamide[10] may be due in part to hydrogen bonding with this solvent. Further work will be required to define the interesting differences between these metallocarboxylate anions.

Reactions of (η-C_5H_5)Re(NO)(CO)H (1). We began our investigation of 1 by attempting some reactions considered characteristic of metal carbonyl hydrides. Although many neutral carbonyl hydrides exhibit significant Lowry–Brønsted acidity, all attempts to deprotonate 1 by using a variety of bases[28] have been unsuccessful. Compound 1 did not react with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) to form a dinitrosyl nor with diazomethane to form the stable[1,6] methyl derivative. In an attempt to abstract hydrogen (H·), 1 was refluxed in benzene for 24 h with dibenzoyl peroxide[29] but was recovered unchanged.

The first reactions found for 1 involved halogenation.[30] Thus, reaction with CBr_4 or Br_2 afforded (η-C_5H_5)Re(NO)(CO)Br (7) as red, air-stable crystals. The bromine reaction gave the bromide in 83% yield, but use of *N*-bromosuccinimide increased the yield to 96%.

These reactions suggested that the behavior of 1 toward other electrophilic reagents should be explored. Our interest in cycloheptatrienyl chemistry[32] suggested tropylium cation ($C_7H_7^+$) as a candidate, and the reaction took place in high yield as shown in eq 5.[33] Evidently 1 serves as a hydride donor to form cycloheptatriene, which coordinates to the 16-electron [(η-C_5H_5)Re(NO)(CO)]$^+$ cation formally produced. A number of metal carbonyl hydrides fairly readily donate hydride to organic substrates, to coordinated organic ligands, or to other transition metals; these processes have been extensively investigated.[34] With a somewhat different emphasis, Beck and Schloter[35] have shown that the strong hydride abstractor trityl cation (Ph_3C^+) affords a useful and perhaps quite general route for transforming L_nMH to L_nMX or $[L_nML']^+$ (where X^- is a lightly stabilizing ligand such as BF_4^- and L′ is a neutral electron-pair donor). For example, the trityl reaction has recently been applied by Legzdins and Martin to (η-C_5H_5)W$(NO)_2$H in acetonitrile solution to obtain [(η-C_5H_5)W$(NO)_2$($NCCH_3$)]$^+$.[36]



(5)

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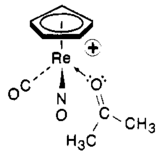
The rhenium hydride 1 also reacts with $Ph_3C^+PF_6^-$ in acetonitrile to give the complex [(η-C_5H_5)Re(NO)(CO)($NCCH_3$)][PF_6] (9) in high yield. Similar reactions in the presence of acetone or THF afford cations 10 and 11, respectively, with triphenylmethane as the only other product. Cations 9–11 as their PF_6^- salts are yellow, air-stable solids. Carbonyl and nitrosyl stretching bands are shifted as expected to higher frequencies, and the NMR resonance of the η-C_5H_5 protons is shifted to lower field as compared with that for 1. These characteristic shifts in IR and NMR parameters have proven extremely useful in the preliminary identification of new compounds.



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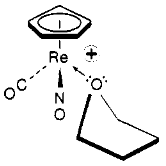

11

Cations 9–11 exhibit ^{1}H NMR signals for coordinated CH_3CN, acetone, and THF which are shifted downfield from the free ligand. In CD_2Cl_2, 9 and 11 show good stability, but the acetone cation slowly decomposes forming free acetone and other unknown products. The ^{1}H NMR spectrum recorded with minimum delay after 10 was dissolved in acetone-d_6 showed (in addition to the η-C_5H_5 resonance) only a signal for free protioacetone; thus there is rapid and reversible ligand dissociation under these conditions. Moreover, when 10 was dissolved in THF and ether added to precipitate the salt, 11 was recovered; similarly a solution of 11 in acetone yielded 10 as the precipitate when ether was added. Both acetone and THF are fairly labile in these cations, but similar experiments with the acetonitrile cation 9 provided no evidence for ligand dissociation or exchange. We point out here that if cations 10 and 11 had static structures corresponding to the sketches, the two sides of the acetone and of the THF would be nonequivalent owing to the chirality at rhenium. In fact, diastereotopic shifts were not observed, most probably due to rapid and reversible ligand dissociation.

The reaction of 1 with trityl cation is an intriguing and synthetically useful process. We have utilized this procedure to prepare a number of other [(η-C_5H_5)Re(NO)(CO)L]$^+$ derivatives which will be described elsewhere. These results, in conjunction with our studies of other metals including the analogous (η-C_5H_5)Os$(CO)_2$ system,[37] suggest that hydride donation may be a general property of carbonyl hydrides. The abstraction reaction raises interesting questions as to the nature of the intermediates which form in the absence of strong donor ligands. We shall address this question in a subsequent paper.[38]

Experimental Section

General Data. All reactions were carried out under a nitrogen atmosphere by using solvents dried by standard procedures and distilled just prior to use. Acetone was dried as follows: reagent acetone was distilled and added to hot (ca. 100 °C) molecular

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(27) We have not yet found conditions under which salts of 5 can be isolated and characterized.

(28) Hydride 1 was resistant to Et_3N, NaN$(SiMe_3)_2$, $KOCMe_3$, KOH–EtOH, and 1,8-bis(dimethylamino)naphthalene ("proton sponge").

(29) At 80 °C, the half-life of dibenzoyl peroxide is ca. 7 h: Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; p 469.

(30) We gratefully acknowledge unpublished work of Dr. R. P. Stewart, Jr., in this department during 1971 and 1972, in which (η-C_5H_5)Re(NO)(CO)X (X = Cl, Br, I) were prepared by reaction of 1 with CCl_4, CBr_4, and SnI_4, respectively. More recently, the iodide has been reported by Legzdins et al.[31]

(31) Hames, B. W.; Kolthammer, B. W. S.; Legzdins, P. *Inorg. Chem.* **1981**, *20*, 650.

(32) Heinekey, D. M.; Graham, W. A. G. *J. Am. Chem. Soc.* **1979**, *101*, 6115; **1982**, *104*, 915.

(33) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1981**, *217*, C37.

(34) Leading references to this work may be found in two recent papers. (a) Bodnar, T.; LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 3292. (b) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *Ibid.* **1981**, *103*, 4415.

(35) Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214.

(36) Legzdins, P.; Martin, D. T. *Inorg. Chem.* **1979**, *18*, 1250.

(37) Hoyano, J. K.; May, C. J.; Graham, W. A. G. *Inorg. Chem.* **1982**, *21*, in press.

(38) Sweet, J. R.; Graham, W. A. G., manuscript in preparation.

sieves (Type 3A); after being cooled it was transferred onto Drierite from which it was distilled immediately before it was required. All glassware was cooled under a nitrogen stream after it was removed from the oven. Rhenium carbonyl (Strem Chemicals), triphenylcarbenium hexafluorophosphate (Aldrich), and tetrafluoroboric acid–diethyl ether complex (Aldrich) were used as received. $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2][BF_4]$ was prepared as earlier described.[6a] Analyses were performed in the Microanalytical Laboratory of this department.

Infrared spectra were measured by using a Nicolet MX-1 instrument. Raman spectra of **1** and **4** were recorded with a Beckman Model 700 Raman spectrometer having a krypton laser operating at 6471 Å; these compounds melt slightly above room temperature, and the liquified samples were contained in sealed capillaries. Mass spectra were obtained by using an A.E.I. MS-12 spectrometer with Kratos DS50 data acquisition system; an ionizing voltage of the customary 70 eV produced spectra that were too complex for easy identification of the fragmentation pattern, and spectra were run at 14–16 eV. NMR spectra were recorded by using a Bruker WH-200 or WH-400 FT spectrometer.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(CO)H$ (1). Triethylamine (2.0 mL, 14 mmol), H_2O (2.0 mL, 111 mol), and $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2][BF_4]$ (2.00 g, 4.71 mmol) were heated in 25 mL of acetone at 50 °C for 1.0 h during which there was vigorous gas evolution. The resulting red solution was extracted with 5 × 20 mL of pentane; the organic layers were combined and the solvents removed under reduced pressure, affording a red oil. After dissolution of the oil in the minimum volume of pentane, drying over $MgSO_4$, and filtering, cooling the solution very slowly to −78 °C gave **1** as orange crystals (1.36 g, 93%): mp 30.5–31.0 °C; IR (hexane, cm^{-1}) 1980 (s, ν_{CO}), 1723 (s, ν_{NO}); ^1H NMR (CD_2Cl_2) δ 5.60 (5 H), −8.50 (1 H, br, see text); mass spectrum (40 °C, 14 eV) M^+, $(M - CO)^+$, $(M - CO - NO)^+$.

Anal. Calcd for $C_6H_6NO_2Re$: C, 23.22; H, 1.95; N, 4.51. Found: C, 23.21; H, 1.96; N, 4.53.

The deuterated analogue, $(\eta\text{-}C_5H_5)Re(NO)(CO)D$ (**4**), was prepared by a similar procedure in acetone-d–D_2O solvent.

Thermal Stability of $(\eta\text{-}C_5H_5)Re(NO)(CO)H$ (1). An analytically pure sample of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (ca. 0.025 g, 0.08 mmol) was placed in a 50-mL, 3-necked flask equipped with nitrogen outlet, a reflux condenser, and a magnetic stir bar. The vessel was evaculated and filled with nitrogen three times. Dried, freshly distilled decane (10 mL) was added and the apparatus immersed in an oil bath (180 °C) until the oil level was slightly below that of the solution.[39] The solution was heated in this manner for 1 week. Periodically, the vessel was removed from the oil bath and cooled briefly, and an infrared sample was removed by syringe against a stream of nitrogen.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(CO)COOH$ (3). Triethylamine was added dropwise to a solution of $[(\eta\text{-}C_5H_5)Re(NO(CO)_2][BF_4]$ (0.50 g, 1.18 mmol) in 10 mL of water to give an orange solution with a yellow precipitate. Addition of $(C_2H_5)_3N$ was continued until precipitation was complete. After the supernatant solution was syringed off, the yellow solid was washed with 3 × 5 mL of H_2O and dried under vacuum, affording **3** (0.30 g, 71%) as yellow microcrystals which darkened and decomposed without melting at about 90 °C: IR (THF, cm^{-1}) 2960 (s, br, ν_{OH}), 1986 (s, ν_{CO}), 1729 (s, ν_{NO}), 1631 (m, ν_{COOH}); ^1H NMR (CD_2Cl_2) δ 5.83 (5 H), 9.47 (br, 1 H); mass spectrum (75 °C, 16 eV) M^+, $(M - OH)^+$, $(M - OH - CO)^+$.

Anal. Calcd for $C_7H_6NO_4Re$: C, 23.73; H, 1.71; N, 3.95. Found: C, 23.70; H, 1.74; N, 3.96.

Protonation of $(\eta\text{-}C_5H_5)Re(NO)(CO)COOH$ (3). Addition of HBF_4–Et_2O to an orange solution of **3** (0.100 g, 2.82 mmol) in CH_2Cl_2 (10 mL) at 0 °C gave a yellow solution from which a yellow solid precipitated. After addition of ether (20 mL) to complete precipitation, the solid was collected, washed with 3 × 10 mL of ether, and dried under vacuum. IR and ^1H NMR showed only peaks expected for **2** (0.110 g, 92%).

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(CO)Br$ (7). *N*-bromosuccinimide (0.290 g, 1.63 mmol) was added to a stirred solution of **1** (0.500 g, 1.61 mmol) in CH_2Cl_2 (50 mL) at room temperature. The initially light orange solution turned dark red, and starting material had been consumed by the time and IR spectrum was run. Solvent was removed at reduced pressure, leaving a dark red solid which was extracted with benzene. The combined extracts were concentrated, placed on a Florisil (100–200 mesh) column, and eluted with benzene. A red band moved quickly down the column and was collected, and the solvent was removed to give **7** as red microcrystals (0.601 g, 96%): mp 133–134 °C; IR (hexane, cm^{-1}) 2003 (s, ν_{CO}), 1742 (s, ν_{NO}); ^1H NMR (CD_2Cl_2) δ 5.86; mass spectrum (90 °C, 16 eV) M^+, $(M - CO)^+$, $(M - CO - NO)^+$.

Anal. Calcd for $C_6H_5BrNO_2Re$: C, 18.51; H, 1.29; N, 3.60. Found: C, 18.51; H, 1.29; N, 3.57.

Reaction of 1 with Bromine and CBr_4. (a) Bromine (0.098 mL, 1.90 mmol) was added dropwise to a solution of **1** (0.500 g, 1.61 mmol) in acetone (25 mL) at 0 °C. After the solution was refluxed in a 60 °C bath for 2 h, solvent removal and workup as described above afforded **7** (0.520 g, 83%), characterized spectroscopically.

(b) CBr_4 (0.22 g, 0.64 mmol) and **1** (0.20 g, 0.64 mmol) were heated at 60 °C in 10 mL benzene for 2 h. Solvent removal and chromatography as above afforded **7** (0.13 g, 52%).

Preparation of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(CH_3CN)][PF_6]$ (9). A solution of $[Ph_3C][PF_6]$ (0.625 g, 1.61 mmol) in CH_3CN (10 mL) was added dropwise to a solution of **1** (0.500 g, 1.61 mmol) in 20 mL of CH_3CN at 0 °C, forming a bright yellow solution. Addition of ether precipitated the product which was collected and washed with 3 × 20 mL of ether, affording **9** as yellow microcrystals (0.750 g, 94%): IR (CH_2Cl_2, cm^{-1}) 2030 (s, ν_{CO}), 1769 (s, ν_{NO}); ^1H NMR (CD_2Cl_2) δ 6.08 (5 H), 2.82 (3 H).

Anal. Calcd for $C_8H_8F_6N_2O_2PRe$: C, 19.40; H, 1.63; N, 5.65. Found: C, 19.47; H, 1.63; N, 5.56.

Preparation of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(acetone)][PF_6]$ (10). A solution of $[Ph_3C][PF_6]$ (0.125 g, 0.32 mmol) in 5 mL of acetone was added dropwise to a 0 °C solution of **1** (0.100 g, 0.32 mmol) in acetone (5 mL), producing a reddish yellow solution. Addition of ether resulted in a precipitate which was washed with 3 × 30 mL of ether to afford yellow microcrystals of **10** (0.055 g, 33%): IR (CH_2Cl_2, cm^{-1}) 2019 (s, ν_{CO}), 1757 (s, ν_{NO}); ^1H NMR (CD_2Cl_2) δ 6.16 (5 H), 2.66 (6 H).

Anal. Calcd for $C_9H_{11}F_6NO_3PRe$: C, 21.10; H, 2.16; N, 2.73. Found: C, 21.29; H, 2.09; N, 2.89.

Preparation of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(THF)][PF_6]$ (11). Dropwise addition of $[Ph_3C][PF_6]$ (0.250 g, 0.64 mmol) in CH_2Cl_2 (12 mL) to a solution of **1** (0.200 g, 0.64 mmol) in THF (8 mL) which was maintained at −15 °C produced a yellow solution and some precipitate. Slow warming to room temperature and addition of ether gave more precipitate which was collected and washed with 3 × 10 mL of ether, affording yellow, microcrystalline **11** (0.250 g, 74%): IR (CH_2Cl_2, cm^{-1}) 2017 (s, ν_{CO}), 1755 (s, ν_{NO}); ^1H NMR (CD_2Cl_2) δ 6.12 (s, 5 H), 4.24 (m, 4 H), 2.12 (m, 4 H).

Anal. Calcd for $C_{10}H_{13}F_6NO_3PRe$: C, 22.82; H, 2.49; N, 2.66. Found: C, 22.56; H, 2.29; N, 2.78.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and for a scholarship to J.R.S. Useful discussions with Dr. P. Legzdins and early investigations by Dr. R. P. Stewart, Jr.[30] are gratefully acknowledged.

Registry No. **1**, 38814-46-9; **2**, 31960-40-4; **3**, 69621-07-4; **4**, 81831-24-5; **7**, 59568-03-5; **9**, 81831-26-7; **10**, 81831-28-9; **11**, 81831-30-3.

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(39) Immersion of the vessel beyond this level results in slow deposition of solid material on the sides of the flask. Direct contact with the heat from the oil bath causes slow decomposition of this material to traces of $(\eta\text{-}C_5H_5)Re(CO)_3$ and a non-carbonyl-containing black solid.