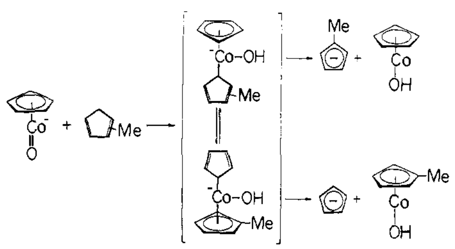
Scheme II



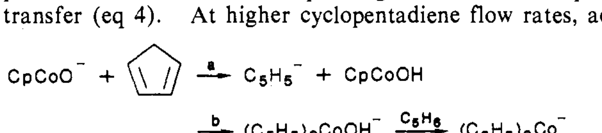
the $CpCo(^{18}OD)(OCH_3)^-$ ion, formed by addition of CH_3OD to $CpCo^{18}O^-$, reacts with H_2O to yield only $CpCo(OH)(OCH_3)^-$, $CpCo(^{18}OD)(OH)^-$, and $CpCo(OH)_2^-$ as primary and secondary products, while $CpCo(OH)(OCH_3)^-$ reacts with CD_3OD to yield $CpCo(OH)(OCD_3)^-$, $CpCo(OCH_3)(OCD_3)^-$, and $CpCo(OCD_3)_2^-$ but no $CpCo(OD)(OCH_3)^-$. Moreover, $CpCo(OCH_3)_2^-$ undergoes consecutive alkoxyl exchanges with CD_3OD to produce $CpCo(OCH_3)(OCD_3)^-$ and $CpCo(OCD_3)_2^-$.

Hydroxyl and alkoxyl group exchange in the reactions of **2** with water or alcohols requires oxidative insertion of cobalt into an O–H bond and formation of a hydridocobalt intermediate **3** possessing equivalent hydroxyl or alkoxyl groups and a "slipped" (η^3 or η^1)-Cp ligand or, alternatively, an η^4-1,3-cyclopentadiene ligand.[9] The stable H_2O adducts formed in the flow reactor with compositions corresponding to **3** are shown to have equivalent hydroxyl groups by the *statistical* yields for H_2O vs $H_2{}^{18}O$ loss from CID of the mixed isotopomers in the triple quadrupole. We also note that the occurrence of H_2O (or CH_3OH) loss as the lowest energy decomposition pathway for these ions argues against an $(\eta^4\text{-}C_5H_6)Co(OR)_3^-$ structure.

Approximately 10% of the reaction between **1** and CH_3OH yields $CpCo(OH)(H)^-$ by dehydrogenation and CH_2O loss. Reaction of $CpCo^{18}O^-$ with CH_3OD in the flow reactor followed by hydroxyl exchange of the dehydrogenation product (m/z 145) with H_2O in the middle quadrupole yields *only* $CpCo(OH)(H)^-$ (m/z 142) and *no* $CpCo(OH)D^-$ (m/z 143) or $CpCo(^{18}OH)H^-$ (m/z 144) (eq 3). This indicates that dehydrogenation of CH_3OD occurs by initial O–D addition across the metal–oxygen bond followed by β-elimination of CH_2O.

$$\underset{m/z\ 142}{CpCo^{18}O^-} \xrightarrow{CH_3OD} \underset{m/z\ 145}{CpCo(^{18}OD)(H)^-} \xrightarrow{H_2O} \underset{m/z\ 142}{CpCo(OH)(H)^-} \quad (3)$$

The reaction of **1** with 1,3-cyclopentadiene provides an especially interesting example of the sequence outlined in eq 1. Two primary products are observed corresponding to addition and proton transfer (eq 4). At higher cyclopentadiene flow rates, addi-



(4a)
(4b)

tion–dehydration occurs to produce a tricyclopentadienylcobalt anion that is best formulated as $(\eta^5\text{-Cp})(\eta^1\text{-Cp})_2Co^-$.[10] Reaction 4a is evidently not just a simple proton transfer, since reaction of **1** with methylcyclopentadiene (MeC_5H_5) yields nearly equal amounts of $MeC_5H_4^-$ and $C_5H_5^-$. Moreover, the mixed adduct $CpCo(OH)(MeC_5H_4)^-$ incorporates a single deuterium when reacted with D_2O and undergoes CID to yield nearly equal amounts of $MeC_5H_4^-$ and $C_5H_5^-$. These observations suggest that the two organic ligands in both the stabilized adduct and the proton transfer intermediate become chemically equivalent, presumably by way of the η^5-to-η^1 haptotropic rearrangement shown in Scheme II.[11] A complete accounting of the reactions of $CpCoO^-$ will be reported in a subsequent publication.

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CO Hydrogenation, Deoxygenation, and C–C Coupling Promoted by $[(silox)_2TaH_2]_2$

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The Fischer–Tropsch (F–T) reaction, considered a potential solution to future energy concerns, has commanded the attention of researchers in both heterogeneous and homogeneous catalysis for the past 15 years.[1–4] The most widely accepted mechanism[2] for this conversion of synthesis gas (CO/H_2) to hydrocarbons and oxygenates incorporates three crucial steps: (1) CO is deoxygenated,[4–10] presumably via dissociative adsorption;[4] (2) H-transfer to surface carbides[2–5] or CO_{ads}[7,11–13] produces surface methylene

† Sloan Foundation Fellow, 1987–1989.

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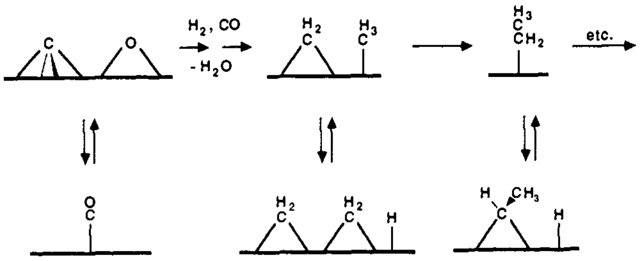
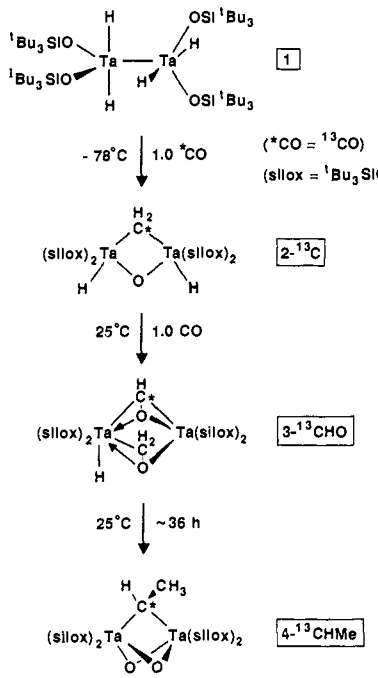
Scheme I



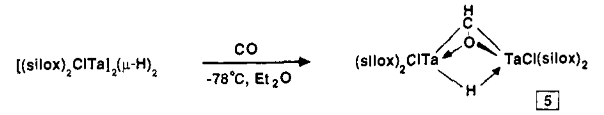
Scheme II



groups;[2,14] (3) C–C bond formation occurs through oligomerization of $(CH_2)_{ads}$ (Scheme I).[2-4,14] Various organometallic species model the individual steps,[5-15] yet fall short of corroborating the entire sequence. Reported herein is the carbonylation of $[(silox)_2TaH_2]_2$ (**1**,[16] silox = t-Bu_3SiO^-)[17] and successive reactions which encompass the critical transformations of the F–T pathway.

When treated with 1.0 equiv of CO at −78 °C, a hexane slurry of orange-brown **1**[16,18] precipitated thermally sensitive, off-white $[(silox)_2TaH]_2(\mu\text{-}O)(\mu\text{-}CH_2)$ (**2**) in 67% yield (Scheme II).[19] Two broad resonances at δ 7.08 and δ 15.99 correspond to the μ-CH_2 group and the terminal hydrides (ν(TaH/D) = 1792/1285 cm^{-1}), respectively. Prepared via **1** and ^{13}CO, **2**-^{13}C manifests a triplet in the ^{13}C NMR at δ 178.10 (J_{CH} = 135 Hz) characteristic of the μ-methylene. When quenched with H_2O, **2** generated 0.9 equiv of CH_4 and 1.8 H_2 upon decomposition.[20] A similar quench with D_2O provided ≥80% CH_2D_2, <20% CH_3D, and a trace of CH_4.[21]

An uptake of 1.0 CO was noted when **2-^{13}C** was exposed to excess carbon monoxide, generating another thermally sensitive, colorless complex, $[(silox)_2TaH](\mu\text{-}^{13}CHO)(\mu\text{-}CH_2O)[Ta(silox)_2]$ (**3-^{13}CHO**),[22] in which the *^{13}C–O bond has reformed.* Doublets (J_{HH} = 3.5 Hz) at δ 2.92 and δ 3.36 characterize the μ-CH_2O fragment, while singlets at δ 5.80 and δ 14.99 are observed for the μ-CHO unit and terminal hydride (ν(TaH/D) = 1774/1274 cm^{-1}), respectively. The ^{13}C NMR spectrum of **3-^{13}CHO/^{13}CH$_2$O** exhibits a doublet (J_{CH} = 166 Hz) at δ 134.94 for the formyl and a "triplet" (J_{CH} = 159 Hz) at δ 79.08 corresponding to the formaldehyde. An aqueous degradation of **3** produced 1.0 H_2 and 2.0 CH_3OH.[23] The structure of **3-^{13}CHO** shown in Scheme II is consistent with NOE experiments,[24] and the spectral data compare favorably with similar molecules[7,8] such as $(silox)_3Ta(\eta^2\text{-}CH_2O)$ (^{13}C NMR: δ 93.87, J_{CH} = 159 Hz)[16] and thermally unstable, colorless $[(silox)_2TaCl]_2(\mu\text{-}H)(\mu\text{-}CHO)$ (**5**, eq 1)[25] prepared from $[(silox)_2TaCl]_2(\mu\text{-}H)_2$[16] and CO at −78 °C (^{13}C NMR: δ 160.3, J_{CH} = 167 Hz). X-ray structural characterization[26] of $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4(\mu\text{-}H)(\mu\text{-}CHO)$ (^{13}C NMR: δ 168, J_{CH} = 168 Hz), prepared by Schrock et al.,[27] provides precedence for the μ-formyls of **3** and **5**. The chloroformyl **5** produced 0.86 equiv of MeOH when decomposed by H_2O and 1.0 H_2 when subjected to HCl.[27]

 (1)

When **3–^{13}CHO** remained at 25 °C in the solid state or in solution for > 2 days, deoxygenation concomitant with C–C bond formation occurred, affording light-yellow, crystalline μ-ethylidene $[(silox)_2Ta]_2(\mu\text{-}O)_2(\mu\text{-}^{13}CHMe)$ (**4-^{13}CHMe**, 61%).[28] A ^{13}C resonance at δ 191.22 ($^1J_{CH}$ = 109, $^2J_{CH}$ = 7 Hz) corresponds to the carbon bridge while the Me group is observed at δ 25.67 ($^1J_{CH}$ = 128, $^2J_{CH}$ = 4 Hz). From synthesis of **4-^{13}CH^{13}CH$_3$**, a typical sp^3–sp^3 coupling ($^1J_{CC}$)[29] of 36 Hz was obtained. The ^{1}H NMR of **4** reveals a doublet at δ 3.81 (Me) and a quartet at δ 5.51 (C*H*Me, ^3J = 7.4 Hz). Exposure of **4** to H_2O effected degradation, providing 1.0 equiv of C_2H_6 (IR). The μ-ethylidene complex **4** may also be prepared by thermolysis of **3** at 60 °C (1 h, hexane); **4** is quite robust, decomposing to give undetermined products at 90 °C.

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(18) The near D_{2d} structure of **1** indicated has been confirmed by X-ray structural studies: Van Duyne, G. D.; Churchill, M. R.; Wolczanski, P. T., unpublished results.
(19) **2**: decomposition $t_{1/2} \sim$ 4 h at 25 °C in benzene; $t_{1/2} \sim$ 12 h in the solid state (25 °C); ^{1}H NMR (C_6D_6) δ 1.28 (s, silox, 27 H); ^{13}C {^{1}H} NMR δ 23.56 (SiC), 30.56 (CH_3).
(20) All measurements of gas release or uptake were conducted via Toepler pump (±5–10%, depending on the scale and purity of reagents).
(21) Determined by MS and confirmed via analysis of an H_2O quench of **2-d_4** which results in CH_2D_2, CD_3H, and CD_4 in approximately the same ratio.
(22) **3**: the transformation to **4** occurs with $t_{1/2} \sim$ 1–2 h at 25 °C in benzene; $t_{1/2} \sim$ 2–3 h in the solid state (25 °C). From **2**, **3** can be isolated in 55% yield; it may be more conveniently prepared from **1** (1.8 CO uptake) in 85% yield: ^{1}H NMR (C_6D_6) δ 1.15, 1.21, 1.30, 1.35 (s, silox, 27 H each); ^{13}C {^{1}H} NMR δ 23.49, 23.64, 23.84, 24.07 (SiC), 30.52, 30.60, 30.86, 31.17 (CH_3). IR spectra of **3**, **3-^{13}CHO**, and **3-^{13}CHO/^{13}CH$_2$O** failed to reveal C–O absorptions, presumably due to overlap with silox bands.
(23) Measured by GC. When quenched with D_2O, the methanol generated was tentatively assigned as a ~1:1 mixture of CHD_2OD and CH_2DOD by ^{13}C NMR.
(24) NOE experiments suggest: (1) the TaH is proximate to the μ-CH_2O unit; (2) one of the μ-CH_2O protons is near the μ-CHO.
(25) **5**: decomposition $t_{1/2} \sim$ 3 h at 25 °C in benzene; $t_{1/2} \sim$ 12 h in the solid state; ^{1}H NMR (C_6D_6) δ 1.24, 1.26, 1.28, 1.36 (s, silox, 27 H each), 6.18 (d, μ-CHO, J_{HH} = 2.8 Hz), 9.56 (d, μ-H, J_{HH} = 2.8 Hz); ^{13}C NMR of **5-^{13}C** δ 23.76, 24.00, 24.32, 25.76 (SiC), 30.39 (CH_3), 160.3 (br, μ-CHO, $^1J_{CH}$ = 167, $^3J_{CH}$ = 3 Hz); IR (Nujol) $\nu(Ta_2H)$ = 1270 (v br) cm^{-1}.
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(28) **4**: ^{1}H NMR (C_6D_6) δ 1.28 (s, silox, 108 H); ^{13}C {^{1}H} NMR δ 23.97 (SiC), 30.53 (CH_3). Anal. Calcd for $Ta_2Si_4O_6C_{50}H_{112}$: C, 46.78; H, 8.79. Found: C, 46.57; H, 8.65. M_r found 1053 (calcd 1284).
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The carbonylation chemistry of $[(\text{silox})_2TaH_2]_2$ (**1**) tracks the critical sequence of complicated reactions pertaining to the F-T mechanism (deoxygenation, H-C and C-C bond formation) and provides alternative views of certain heterogeneous transformations. Since **2** is formed directly, the generation of $(CH_2)_{ads}$ via H-transfer concomitant with or prior to C-O bond scission must still be considered;[30] the dissociative adsorption of CO may not be necessary. Most importantly, a C-O bond has been broken, reformed, and broken again in the conversion of **1** to **4**.[31] Extrapolating to heterogeneous processes, oxygenated surfaces may serve as reservoirs for CH, CH_2, and, presumably, CH_3[32] functionalities via $(OCH)_{ads}$,[33] $(OCH_2)_{ads}$,[34] and $(OCH_3)_{ads}$. Methylene units adsorbed on actual F-T surfaces are therefore *not constrained to be solely metal-bound.* Further mechanistic studies and characterizations of thermal, hydrogenation, and other carbonylation products are currently being undertaken.

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(32) In view of ref 31, the conversion of **3** to **4** may proceed via the following: (1) reductive elimination to form a μ-OCH_3; (2) oxidative addition of the O-CH_3 bond, generating a Ta-CH_3; (3) Me transfer to μ-CHO concomitant with deoxygenation.

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A General Class of Stable Alkyl Halide Complexes: Synthesis, Structure, and Reactivity of Alkyl Iodide Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IR)]^+BF_4^-$

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Of all of the common organic functional groups, alkyl halides (RX) have by far the least developed coordination chemistry.[1-3] To our knowledge isolable 1:1 adducts are unknown, although the *bis*(methyl iodide) complex $[(H)_2Ir(PPh_3)_2(ICH_3)_2]^+X^-$ has been recently described by Crabtree.[1] The lack of stable alkyl halide complexes has generally been attributed to poor Lewis basicity and/or the availability of facile decomposition pathways such as oxidative addition. In this communication, we report the synthesis and isolation of alkyl iodide complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IR)]^+BF_4^-$ and other data that suggest that alkyl halide complexes may be far more accessible than previously realized. Importantly, the coordination of alkyl halides to metals provides a new generation of leaving groups that can be easily modified and, as in the reported examples, rendered chiral.

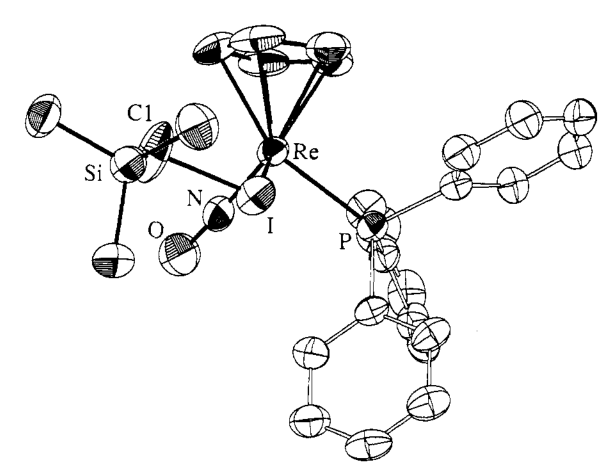

Figure 1. Structure of the cation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2Si(CH_3)_3]^+BF_4^-\cdot(CH_2Cl_2)_{0.5}$ (**4d**$\cdot(CH_2Cl_2)_{0.5}$). Selected bond lengths (Å) and angles (deg): Re-I, 2.678 (1); Re-P, 2.385 (3); Re-N, 1.740 (9); N-O, 1.20 (1); I-Cl, 2.18 (1); Cl-Si, 1.88 (2); I-Re-P, 91.82 (9); I-Re-N, 97.0 (4); P-Re-N, 91.1 (3); Re-N-O, 177 (1); Re-I-Cl, 102.5 (5); I-Cl-Si, 114.5 (9).

We recently reported that the reaction of methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) and $HBF_4\cdot Et_2O$ (CH_2Cl_2, -78 °C) gave a reactive intermediate (stable to -20 °C) formulated as the chiral pyramidal Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+BF_4^-$ (**2**) or the CH_2Cl_2 adduct $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+\ BF_4^-$ (**3**).[4] Subsequent ^{13}C NMR experiments have provided good evidence for coordinated CH_2Cl_2.[4b] Hence, the reaction of **1** and $HBF_4\cdot Et_2O$ was followed by addition of alkyl iodides RI (3.0 equiv, Scheme I). New products formed upon warming (-40 to 0 °C, ca. 95%, ^{31}P NMR). Workup gave alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IR)]^+BF_4^-$ (**4**; R = CH_3 (**a**), CH_2CH_3 (**b**), $CH_2CH_2CH_3$ (**c**), $CH_2Si(CH_3)_3$ (**d**)) as analytically pure powders in 67-87% yields.[5] The structures of **4a-d** followed from their spectroscopic properties and in particular from the downfield shifts exhibited by the ICH carbons and protons in ^{13}C and ^1H NMR spectra.[5] Oxidative addition products such as $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)(Br)]^+X^-$ show upfield ReCH ^1H and ^{13}C NMR resonances that are also strongly coupled to phosphorus.[6]

Crystals of the solvate **4d**$\cdot(CH_2Cl_2)_{0.5}$ were grown from CH_2Cl_2/hexanes, and the X-ray structure was determined (Figure 1) as described in the Supplementary Material. The carbon-iodine bond (2.18 (1) Å) is very slightly longer than that in ethyl iodide (2.139 (5) Å),[7] and the Re-I bond (2.678 (1) Å) is shorter than

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(2) For chelating aryl halide complexes $o\text{-}C_6H_4X(DL_n)$ ($DL_n = PAr_2$, S, Br, I), see ref 1 and the following: (a) Burk, M. J.; Crabtree, R. H.; Holt, E. M. *Organometallics* **1984**, *3*, 638. (b) Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2913. (c) Barcelõ, F.; Lahuerta, P.; Ubeda, M. A.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M. *J. Chem. Soc., Chem. Commun.* **1985**, 43. (d) Solans, X.; Font-Altaba, M.; Aguilõ, M.; Miravitlles, C.; Besteiro, J. C.; Lahuerta, P. *Acta. Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 841. (e) Cotton, F. A.; Lahuerta, P.; Sanau, M.; Schwotzer, W.; Solana, I. *Inorg. Chem.* **1986**, *25*, 3526. (f) Kulawiec, R. J.; Holt, E. M.; Lavin, M.; Crabtree, R. H. *Ibid.* **1987**, *26*, 2559. (g) Catala, R. M.; Cruz-Garritz, D.; Hills, A.; Hughes, D. L.; Richards, R. L.; Sosa, P.; Torrens, H. *J. Chem. Soc., Chem. Commun.* **1987**, 261.

(3) (a) A diene-chelated cyclopropyl bromide complex has recently been reported: Liotta, F. J., Jr.; Van Duyne, G.; Carpenter, B. K. *Organometallics* **1987**, *6*, 1010. (b) See, also: Cotton, F. A.; Ilsley, W. H.; Kaim. W. *J. Am. Chem. Soc.* **1980**, *102*, 3475.

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(5) All new compounds were characterized by microanalysis, IR, and NMR (^1H, ^{13}C, ^{31}P) as described in the Supplementary Material. Selected NMR data (CD_2Cl_2) for **4b**, **10b** (-60 °C), and **11b** (-40 °C): ^1H NMR (δ) 5.62, 5.56, 5.59 (s, C_5H_5), 3.77, 4.18, 4.43 (dq, J = 9, 7 Hz, C*H*H'), 3.46, 3.73, 3.92 (dq, J = 9, 7 Hz, CH*H'*), 1.65, 1.62, 1.54 (t, J = 7 Hz, CH_3); ^{13}C NMR (ppm) 92.1, 91.9, 91.5 (s, C_5H_5), 24.0, 56.7, 69.9 (d, J = 3.1, ≤2.0, 1.8 Hz, CH_2), 18.8, 17.8, 17.5 (s, CH_3); ^{31}P (ppm) 11.8, 12.9, 13.6 (s); NMR of ICH_2CH_3 (CD_2Cl_2) ^1H NMR (δ) 3.20 (q, J = 7.5 Hz, CH_2), 1.82 (t, J = 7.5 Hz, CH_3); ^{13}C NMR (ppm) 20.89 (s, CH_3), -0.23 (s, CH_2).

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