Polyhedron Vol. 10, No. 16, pp. 1903–1909, 1991
Printed in Great Britain

0277–5387/91 $3.00+.00
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SYNTHESIS AND CHEMISTRY OF SECONDARY ALKYL IODIDE COMPLEXES OF THE FORMULA $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICHRR')]^+BF_4^-$

ALAIN IGAU and J. A. GLADYSZ*

Department of Chemistry, University of Utah, Salt Lake City, UT 84112, U.S.A.

(*Received* 4 *April* 1991; *accepted* 16 *May* 1991)

Abstract—Reactions of deuterodichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCD_2Cl)]^+BF_4^-$ with (**a**) isopropyl iodide, (**b**) *sec*-butyl iodide, (**c**) cyclopentyl iodide, and (**d**) cyclohexyl iodide give secondary alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICHRR')]^+BF_4^-$ (**3a–d**) in good to high NMR yields, depending upon the quantity of alkyl iodide employed. These compounds are much less stable than analogous primary alkyl iodide complexes, but analytically pure **3d** can be isolated from the reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ and $HBF_4\cdot OEt_2$ in neat cyclohexyl iodide (73%). Complex **3d** decomposes in CD_2Cl_2 to give cyclohexyl fluoride, cyclohexene (74% total) and bridging halide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2X^+BF_4^-$ (X = I, 33%; Cl, 36%). The formation of cyclohexyl fluoride suggests BF_4^- participation in carbon–iodine bond cleavage. Reaction of **3d** and PPh_3 gives the substitution product $[Ph_3PC_6H_{11}]^+BF_4^-$ (24%), cyclohexyl fluoride (24%), cyclohexene (30%) and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**7**, 95%). An analogous reaction of **3d** and PPN^+Br^- gives cyclohexene (57%) and **7** (99%).

Stable complexes of alkyl halides and transition metals are scarce.[1–5] Since Crabtree prepared the iridium methyl iodide complexes $[(H)_2Ir(PPh_3)_2(ICH_3)_2]^+X^-$ in pure form a decade ago, the vast majority of adducts isolated have been *primary* alkyl halides. Coordinated alkyl halides have been shown to be dramatically activated towards nucleophilic attack.[1,2,4] Thus, useful applications of secondary and tertiary alkyl halide complexes are readily envisioned. Further, when the metal fragment and alkyl halide are both chiral, there is the possibility that one alkyl halide enantiomer might selectively bind ("chiral recognition").

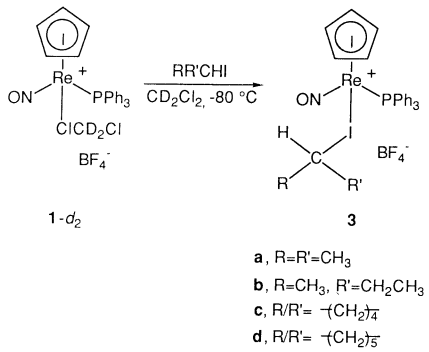
We have previously studied the synthesis, structure and reactivity of the chiral rhenium primary alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2R)]^+BF_4^-$ in detail.[4] With few exceptions, these compounds are easily isolated in pure form and in good to high yields from reactions of the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**1**) and alkyl iodides (3–5 equiv.). We therefore sought to systematically define the scope of analogous secondary and tertiary alkyl iodide complexes that can be generated and/or isolated, and to compare their physical and chemical properties with those of the primary alkyl iodide complexes.

* Author to whom correspondence should be addressed.

RESULTS

(1) *Synthesis of secondary alkyl iodide complexes*

The methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**)[6] and an internal standard were dissolved in CD_2Cl_2 in an NMR tube and treated with $HBF_4\cdot OEt_2$ at −80°C. The generation of the previously reported deuterodichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCD_2Cl)]^+BF_4^-$ (**1**-d_2)[5a] was verified by ^1H and ^{31}P NMR (−60°C). The sample was then frozen in liquid nitrogen and treated with 2 equiv. of (**a**) isopropyl iodide, (**b**) *sec*-butyl iodide, (**c**) cyclopentyl iodide and (**d**) cyclohexyl iodide, as shown in Scheme 1. These mixtures were warmed to −40°C in the NMR probe. Secondary alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICHRR')]^+BF_4^-$ (**3a–d**) formed in 65–75% yields relative to a ^1H NMR resonance of the standard.

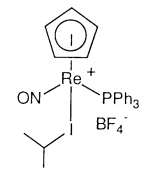
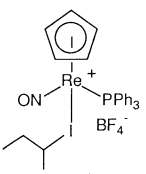
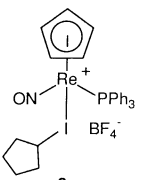
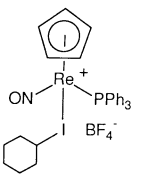


Scheme 1. Synthesis of secondary alkyl iodide complexes **3**.

When larger excesses of secondary alkyl iodides were employed, yields of **3a–d** were somewhat greater. However, extensive efforts to isolate pure complexes by this route were unsuccessful. Therefore, **3a–d** were characterized *in situ* by ^1H, ^{13}C and ^{31}P NMR spectroscopy, as summarized in Table 1. Properties were similar to those found earlier for primary alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2R)]^+BF_4^-$.[4] The ICH ^{13}C NMR resonances (47.9–58.3 ppm) showed diagnostic downfield shifts (22–29 ppm)[7] from those of the free alkyl iodides. The *sec*-butyl complex **3b**, which contains two stereocentres, gave two sets of resonances of equal intensity. Thus, the two possible rhenium/carbon configurational diastereomers formed in equal amounts.

Alternative routes to pure samples of **3** were sought. Thus, the methyl complex **2** was dissolved in *neat* cyclohexyl iodide and treated with $HBF_4 \cdot OEt_2$ at $-40°C$. Workup gave the cyclo-

Table 1. NMR characterization of secondary alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICHRR')]^+BF_4^-$ (**3**)

Complex	^1H NMR (δ)[a]	$^{13}C\{^1H\}$ NMR (ppm)[b]	$^{31}P\{^1H\}$ NMR (ppm)[c]
 **3a**	7.50–7.22 (m, $3C_6H_5$), 5.59 (s, C_5H_5), 4.44 (sept, J = 6.6, CHI), 1.74 (d, J = 6.6, CH_3), 1.72 (d, J = 6.6, $C'H_3$).	PPh_3 at: 133.2 (d, J = 11.4, *o*), 132.5 (d, J = 57.6, *i*), 131.6 (d, J = 2.5, *p*), 129.0 (d, J = 13.0, *m*); 91.6 (s, C_5H_5), 47.9 (d, J = 2.8, CH), 28.0 (s, CH_3), 27.7 (s, $C'H_3$).	12.20 (s)
 **3b**[d]	7.51–7.22 (m, $3C_6H_5$), 5.57 (s, C_5H_5), 4.41/4.33 (m, CHI), 1.74/1.71 (d, J = 7.1, CH_3CH), 1.68 (m, CHH'), 1.01/1.00 (t, J = 7.0, CH_3CH_2).	PPh_3 at: 133.2 (d, J = 10.9, *o*), 132.6 (d, J = 57.0, *i*), 131.6 (d, J = 2.7, *p*), 129.1 (d, J = 10.9, *m*); 91.6/91.5 (d, C_5H_5), 58.3/58.2 (d, J = 2.6, CH), 33.9/32.9 (s, CH_2), 25.4/25.0 (s, CH_3CH), 13.6/12.4 (s, CH_3CH_2).	13.03/12.98 (s)
 **3c**	7.52–7.24 (m, $3C_6H_5$), 5.58 (s, C_5H_5), 4.64 (m, CHI), 2.00 (m, 4H), 1.78 (m, 2H), 1.59 (m, 2H).	PPh_3 at: 133.6 (d, J = 9.4, *o*), 132.2 (d, J = 58.7, *i*), 131.3 (d, J = 2.5, *p*), 128.8 (d, J = 10.8, *m*); 91.4 (s, C_5H_5), 57.1 (s, CH), CH_2 (s) at 37.1, 36.7, 27.2, 22.8.	12.09 (s)
 **3d**	7.49–7.18 (m, $3C_6H_5$), 5.57 (s, C_5H_5), 4.45 (m, CHI), 2.30 (m, 2H), 1.87 (m, 2H), 1.50 (m, 3H), 1.20 (m, 3H).	PPh_3 at: 133.2 (d, J = 11.0, *o*), 132.6 (d, J = 57.4, *i*), 131.7 (s, J = 2.0, *p*), 129.3 (d, J = 10.8, *m*); 91.6 (s, C_5H_5), 54.5 (s, CH), CH_2 (s) at 38.8, 37.1, 27.1, 27.0, 25.5.	12.15 (s)

[a] Recorded at 300 MHz in CD_2Cl_2 at $-40°C$ and referenced to internal $CHDCl_2$ (5.32 ppm). All coupling constants are to ^1H and are in Hz.

[b] Recorded at 75 MHz in CD_2Cl_2 at $-40°C$ and referenced to CD_2Cl_2 (53.8 ppm). All couplings are to ^{31}P and are in Hz. Assignments of phenyl carbon resonances were made as described in footnote c of Table 1 in ref. 8.

[c] Recorded at 121 MHz (unlocked) in CD_2Cl_2 at $-40°C$ and referenced to external 85% H_3PO_4.

[d] Two diastereoisomers in a 50 : 50 ratio.

hexyl iodide complex **3d** in a 73% yield as an analytically pure, tan powder. An IR spectrum (CH_2Cl_2, $-42°C$) showed a ν(NO) at 1707 cm^{-1} (vs). This sample was used for all reactions described below.

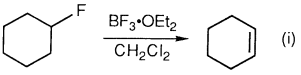
The chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ is sometimes superior to **1** as a precursor to complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$.[5b] Analogous NMR-monitored reactions could not be conducted due to the precipitation of secondary alkyl iodide complexes (**3**) from the chlorobenzene solvent. However, a sample of isopropyl iodide complex **3a** was isolated from a preparative experiment. It was quite pure by ^1H and ^{31}P NMR, but not by microanalysis.

(2) *Thermal and substitution chemistry of cyclohexyl iodide complex* **3d**

A CD_2Cl_2 solution of **3d** and an internal standard was kept at room temperature in an NMR tube. Over the course of 2 days, conversion to two cyclopentadienyl-containing products was observed, as shown in Scheme 2. These were identified, on the basis of ^1H, ^{13}C and ^{31}P NMR spectra, as the previously characterized bridging iodide complex (RR,SS)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2I^+BF_4^-$ (**4**)[9] and bridging chloride complex (SS,RR)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ (**5**).[5a] Yields were 33% and 36%, respectively, relative to an ^1H NMR resonance of the standard. In separate experiments, **4** and **5** were isolated.

The organic products derived from **3d** were assayed by ^1H NMR and gas chromatography (GLC). A mixture of cyclohexyl fluoride (δ 4.65, CHF) and cyclohexene (δ 5.87, =CH) was formed. No cyclohexyl iodide was detected. With time, the cyclohexyl fluoride diminished as the amount of cyclohexene increased until, at the end of 2 days, only cyclohexene (74%) remained.

An authentic sample of cyclohexyl fluoride was treated with $BF_3 \cdot OEt_2$ in CD_2Cl_2 at room temperature. Clean conversion to cyclohexene occurred over the course of 8 h, as assayed by ^1H NMR and GLC [eq. (1)]. However, cyclohexyl iodide and $BF_3 \cdot OEt_2$ did not react after 24 h under analogous conditions.



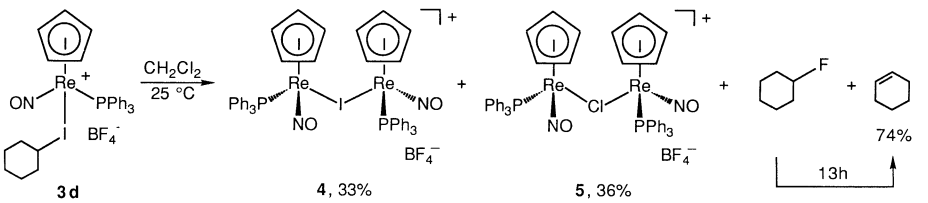
Next, a CD_2Cl_2 solution of **3d** and an internal standard was treated with CH_3CN (1.5 equiv.) at $-80°C$. The sample was warmed to room temperature. Over the course of 12 h, the acetonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ (**6**)[5a] formed as the only cyclopentadienyl and PPh_3-containing product, as assayed by ^1H and ^{31}P NMR. The yield was 80% relative to a ^1H NMR resonance of the standard. However, no cyclohexyl iodide was detected by ^1H NMR or GLC, rather, cyclohexene (87%) was the exclusive organic product. Some cyclohexyl fluoride was detected by GLC during the early stages of the reaction, but it subsequently converted to cyclohexene.

(3) *Reactions of cyclohexyl iodide complex* **3d** *and nucleophiles*

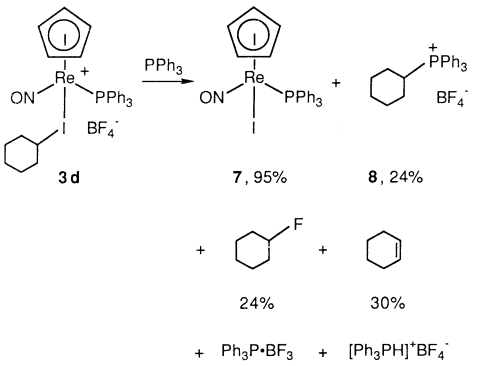
A CD_2Cl_2 solution of **3d** and an internal standard was frozen in liquid nitrogen. PPh_3 (1.4 equiv.) was then added, and the sample was gradually warmed to 0°C. After 8 h, the iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**7**)[10] had formed in a 95% yield, as assayed by ^1H and ^{31}P NMR and shown in Scheme 3. However, three major cyclohexyl-derived products were present: the phosphonium salt $[Ph_3PC_6H_{11}]^+BF_4^-$ (**8**, 24%), cyclohexyl fluoride (24%) and cyclohexene (30%). The ratio of cyclohexyl fluoride and cyclohexene did not change significantly with time.

An authentic sample of **8** was prepared from the previously characterized bromide salt $[Ph_3PC_6H_{11}]^+Br^-$,[11] as described in the Experimental. Also, cyclohexyl iodide and PPh_3 (2 equiv.) did not independently react in CH_2Cl_2 at room temperature (24 h). This shows that the cyclohexyl iodide ligand in **3d** is activated towards attack by PPh_3.

Two additional phosphorus-containing products were evident in the ^{31}P NMR spectrum of the **3d**/PPh_3 reaction mixture. These were not quanti-



Scheme 2. Thermal decomposition of cyclohexyl iodide complex **3d**.



Scheme 3. Reaction of cyclohexyl iodide complex **3d** and PPh_3.

fied, but were assigned as $[Ph_3PH]^+BF_4^-$ (4.45 ppm, d, J(PH) 527.0 Hz) and $Ph_3P \cdot BF_3$ (−5.01 ppm, br, s). The large coupling in the former is diagnostic of a phosphonium salt phosphorus–hydrogen bond.[12] Also, the fluorosulphate analogue $[Ph_3PH]^+FSO_3^-$ has been previously shown to give a similar ^{31}P NMR resonance (CCl_4: 5.4 ppm, d, J(PH) 510 Hz).[13] Accordingly, when a CD_2Cl_2 solution of PPh_3 was treated with $HBF_4 \cdot OEt_2$ (0.7 equiv.), a 4.5 ppm doublet was cleanly generated. The Lewis acid/base adduct $Ph_3P \cdot BF_3$ has also been previously characterized.[14] When a CD_2Cl_2 solution of PPh_3 was analogously treated with $BF_3 \cdot OEt_2$, a broad resonance appeared at −5.0 ppm.

Next, a similar reaction was conducted with **3d** and PPN^+Br^-.[15] The mixture was kept at −40°C for 12 h, and then assayed by ^1H and ^{31}P NMR at room temperature. The iodide complex **7** formed in a 99% yield. However, cyclohexene (57%) was the only organic product detected. An aliquot of the mixture was taken when the sample was at −40°C and analysed by GLC. Some cyclohexyl flouride was present.

(4) *Reactions with tertiary alkyl iodides*

A "less bulky", bridgehead tertiary alkyl iodide was sought for scout experiments. Thus, 1-adamantyl iodide (3 equiv.)[16] was reacted with **1**-d_2 in the presence of an internal standard, as described for the secondary alkyl iodides above. Over the course of several hours at −40°C, a multitude of products formed. The major species (*ca* 20%) exhibited plausible NMR resonances for a 1-adamantyl iodide complex (−20°C: ^1H NMR, δ 5.57, s; ^{31}P NMR 12.1 ppm, s). When the sample was warmed to room temperature, bridging halide complexes **4** (δ 5.42, 49%) and **5** (δ 5.41, 40%) formed. The significant yield of bridging iodide complex **4** also suggests that an appreciable amount of the target complex was generated.

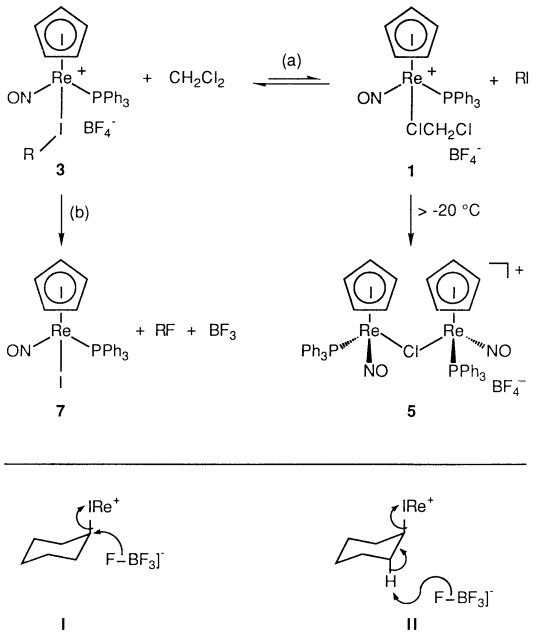
DISCUSSION

We previously reported that isopropyl iodide is about 50% as reactive as methyl iodide, and 67% as reactive as ethyl iodide towards the dichloromethane complex **1** at −41°C.[4a] Thus, secondary alkyl iodides are less nucleophilic than primary alkyl iodides, or poorer Lewis bases in a kinetic sense. This follows logically from their increased bulk. Secondary alkyl iodides are likely poorer Lewis bases in the conventional thermodynamic sense as well. We attempted to demonstrate this by treating cyclohexyl iodide complex **3d** with ethyl iodide (3 equiv.) in CD_2Cl_2 at 0°C. However, the previously characterized[4a] ethyl iodide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2CH_3)]^+BF_4^-$ was not detected by ^1H or ^{31}P NMR. Rather, the independent decomposition of **3d** occurred.

The isolation of secondary alkyl iodide complexes **3** from preparations involving dichloromethane solvent is in all cases complicated by the formation of the bridging halide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2X^+BF_4^-$. The probable key features of these competing decomposition pathways are sketched in Scheme 4. First, solvolytic displacement of the alkyl iodide ligands in **3** can occur to give dichloromethane complex **1** [step (a)], which rapidly decomposes to the bridging chloride complex **5** above −20°C.[5a] This substitution is likely faster and less endothermic than for the corresponding primary alkyl iodide complexes, accounting for the observed stability trend.

Secondly, carbon–iodine bond cleavage can occur to give the iodide complex **7** [step (b)]. Complex **7** can in turn react with **3** or **1** to give bridging iodide complex **4**.[9] The formation of cyclohexyl fluoride in Scheme 2 suggests that the weakly coordinating[17] BF_4^- anion can participate in the carbon–iodine bond cleavage step, as sketched in **I** (Scheme 4). Alternatively, the carbon–iodine bond might undergo heterolysis, and the carbocation of the resulting intimate "ion pair" could react with BF_4^-. Since some cyclohexene seems to form directly from **3d**, it is also possible that BF_4^- serves as the base in an E2 elimination step, as shown in **II**.

The attack of BF_4^- upon coordinated dichloromethane has been proposed as a key step in the decomposition of **1** to bridging chloride complex **5**.[5a] However, the expected primary product FCH_2Cl could not be conclusively identified in the reaction mixture. Thus, the formation of cyclohexyl



Scheme 4. Some possible decomposition pathways for alkyl iodide complexes **3**.

fluoride from **3d** provides welcome precedent for this step. The anion PF_6^- has been shown to be a poorer fluoride ion donor than BF_4^-.[17] Thus, PF_6^- salts of **3** would likely be somewhat more stable. However, $HPF_6 \cdot OEt_2$, which is required for the formation of the precursor dichloromethane complex, no longer appears to be commercially available in adequate purity.

The mass balance for the organic and inorganic decomposition products of **3d** is only fair. Note that steps **I** and **II** (Scheme 4) give the strong acids BF_3 and HF. These in turn can likely react with many of the primary products. Also, the iodide complex **7** has been shown to undergo a "transalkylation" reaction with dichloromethane complex **1** to give the iodochloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2Cl)]^+BF_4^-$.[9]

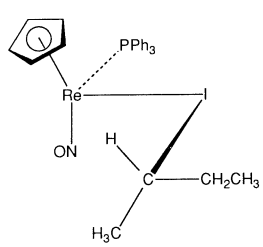
In the reaction of **3d** and PPh_3 (Scheme 3), PPh_3 serves both as a nucleophile (to give phosphonium salt **8**) or a base (to give cyclohexene). Pathways analogous to **I** and **II** (Scheme 4) are likely involved. The formation of comparable amounts of cyclohexyl fluoride and **8** suggests that BF_4^- and PPh_3 attack upon the cyclohexyl iodide ligand is competitive. The BF_3 by-product from the former process subsequently binds to PPh_3, therefore, cyclohexyl fluoride does not convert to cyclohexene as in Scheme 2 and eq. (1). Interestingly, cyclohexyl bromide and PPh_3 react to give the phosphonium salt $[Ph_3PC_6H_{11}]^+Br^-$, without any significant amount of competing elimination.[11]

In contrast to PPh_3, PPN^+Br^- appears to function chiefly as a base towards **3d**. However, the formation of cyclohexene (87%) in the reaction of **3d** and acetonitrile is more surprising. Analogous primary iodide complexes and acetonitrile react to give mainly simple substitution products—acetonitrile complex **6** (82–87%) and free alkyl halides (72–82%).[4a] This suggests a more complex mechanistic sequence, possibly involving the BF_4^- anion, with **3d**.

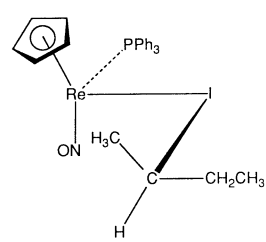
Crabtree has previously reported the isolation of chiral ruthenium isopropyl iodide and cyclohexyl iodide complexes $[(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(ICHRR)]^+PF_6^-$.[2c] He finds that the former undergoes clean reactions with chloride ions to give isopropyl chloride, and pyridine to give the corresponding pyridinium salt. However, the latter gives only cyclohexene upon reactions with nucleophiles. Cyclohexyl halides are well-known to be more susceptible to elimination reactions than acyclic analogues.

We have previously shown that the methyl iodide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_3)]^+BF_4^-$ exchanges only slowly with CD_3I (15 equiv.) in CD_2Cl_2 at room temperature.[4a] Also, the diastereotopic methyl groups of isopropyl iodide complex **3a** give distinct ^1H and ^{13}C NMR resonances (Table 1). These would be equivalenced by any rapid dissociative process. Thus, the reactions in Scheme 1 are probably under kinetic control.

This is likely relevant to the lack of diastereoselectivity in the formation of *sec*-butyl iodide complex **3b**. Based upon crystal structures of a primary alkyl iodide complex and bridging iodide complex **4**,[4a,9] the diastereomers of **3b** likely adopt the structures **III** and **IV**. In each, the large *C*—I



III (*RS,SR*)
(favored, CH_3 and C_5H_5 *anti*)



IV (*RR,SS*)
(disfavored, CH_3 and C_5H_5 *syn*)

substituent, ethyl, is oriented *anti* to the I—Re bond. We had expected **III** to be more stable due to reduced steric interactions between the cyclopentadienyl ligand and the remaining *C*—I substituents. An analogous consideration accounts for the very high diastereoselectivity in the formation of bridging halide complexes **4** and **5**.[9] Thus, we speculate that significant diastereoselection might be realized under thermodynamically controlled conditions.

In summary, this study has established that secondary alkyl iodide complexes (**3**) can be synthesized and in some cases isolated in pure form. However, they are considerably more labile than analogous primary alkyl iodide complexes. Although the cyclohexyl iodide ligand in **3d** is activated towards nucleophilic attack, competing reactions involving the BF_4^- anion are observed and elimination products usually dominate.

EXPERIMENTAL

General

All reactions were conducted under a dry nitrogen atmosphere. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. NMR spectra were recorded on Varian XL-300 spectrometers. The following chemical shift standards were used: ^{1}H, residual $CHDCl_2$ (δ 5.32); ^{13}C, CD_2Cl_2 (53.8 ppm); ^{31}P, external 85% H_3PO_4 (0.00 ppm). Mass spectra were obtained on a VG 770 spectrometer. Analytical gas–liquid chromatography (GLC) was conducted on a Hewlett Packard 5890 chromatograph utilizing a capillary column (cross-linked 5% phenyl methyl silicone, 25 m × 0.2 mm × 0.33 mm film) and a 0.6 cm^3 min^{-1} helium flow. Microanalyses were conducted by Atlantic Microlab. Melting points were determined in evacuated capillaries.[18]

Solvents, reagents and standards were utilized as follows: CH_2Cl_2 and CH_3CN, distilled from P_2O_5; hexane, distilled from sodium; methanol, distilled from magnesium; CD_2Cl_2, distilled from CaH_2; $HBF_4 \cdot OEt_2$ (Aldrich), standardized as described previously;[5a] alkyl iodides (Aldrich), filtered through a 3.5 cm alumina column, distilled, and stored at −10°C over copper in the dark; PPh_3 (Aldrich), recrystallized from benzene; Ph_3SiCH_3 (Pfaltz & Bauer), $BF_3 \cdot OEt_2$, and $AgBF_4$ (Aldrich), used as received; cyclohexyl flouride (Pfaltz & Bauer) was assayed by GLC and returned to the vendor unless pure. The salt[15,19] PPN^+Br^- and 1-adamantyl iodide[16] were prepared by literature procedures.

Isolation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IC_6H_{11})]^+ BF_4^-$ (**3d**). A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**2**;[6] 0.339 g, 0.612 mmol), cyclohexyl iodide (3 cm^3), and a stir bar. The mixture was gently warmed to solubilize **2**, and then cooled to −40°C (CH_3CN/dry ice). Then $HBF_4 \cdot OEt_2$ (0.085 cm^3, 0.67 mmol) was added with stirring. The mixture was kept at −40°C for 50 min and then hexane was added. A precipitate formed, which washed with hexane (2 × 3 cm^3) and dried *in vacuo* to give **3d** as a tan powder (0.374 g, 0.447 mmol, 73%), m.p. 100–105°C, dec. Mass spectrum [(+)-FAB (7 kV, Ar, 3-nitrobenzyl alcohol/$CHCl_3$), *m/z* (relative intensity), ^{187}Re]: 754 (M^+, 24%), 671 (M^+-C_6H_{11}, 41%), 544 (M^+-IC_6H_{11}, 57%). Found: C, 41.6; H, 3.8. Calc. for $C_{29}H_{21}BF_4INOPRe$: C, 41.4; H, 3.7%.

Solutions of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICHRR')]^+ BF_4^-$ (**3**). The following procedure is representative. A 5 mm NMR tube was charged with **2** (0.0453 g, 0.0811 mmol), Ph_3SiCH_3 as a standard (0.0176 g, 0.0641 mmol) and CD_2Cl_2 (0.8 cm^3), and was capped with a septum. The tube was cooled to −80°C, and $HBF_4 \cdot OEt_2$ (0.008 cm^3, 0.073 mmol; 0.85–0.90 equiv.) was added. Next, ^{1}H and ^{31}P NMR spectra were acquired at −60°C, and showed the formation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCD_2Cl)]^+$ (**1**-d_2) in an 85% yield, based upon limiting $HBF_4 \cdot OEt_2$. The sample was frozen in liquid nitrogen, and isopropyl iodide (0.0124 cm^3, 0.124 mmol, 2 equiv.) was added. The tube was slowly warmed to −60°C. Then ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded (negligible reaction). The sample was kept for 8–10 h at −40°C. Subsequent NMR spectra showed the formation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH(CH_3)_2)]^+BF_4^-$ (**3a**, 0.047 mmol relative to the Ph_3SiCH_3 ^{1}H NMR resonance) in a 75% yield based upon **1**-d_2. Table 1 shows the data obtained.

Decomposition of **3d**. A 5 mm NMR tube was charged with **3d** (0.0183 g, 0.0218 mmol), Ph_3SiCH_3 as a standard (0.0123 g, 0.0448 mmol) and CD_2Cl_2 (0.80 cm^3), and was capped with a septum. The tube was kept at room temperature and ^{1}H and ^{31}P NMR spectra were periodically recorded. After 48 h, no **3d** remained. The yields of (*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2I^+BF_4^-$ (**4**, 0.0072 mmol, 33%),[9] (*SS,RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ (**5**, 0.0078 mmol, 36%)[5a] and cyclohexene (0.0083 mmol, 74%) were determined by integration of ^{1}H NMR resonances (C_5H_5, =CH vs Ph_3SiCH_3). The cyclohexene yield was confirmed by GLC. See text for other data.

Reaction of **3d** *and acetonitrile*. A 5 mm NMR tube was charged with **3d** (0.0438 g, 0.0521 mmol), Ph_3SiCH_3 standard (0.0157 g, 0.0599 mmol), and was capped with a septum. The sample was cooled to −80°C, and CD_2Cl_2 (0.8 cm^3) and CH_3CN (0.0040 cm^3, 0.078 mmol) were added via a syringe. The sample was warmed to room temperature, and ^{1}H and ^{31}P NMR spectra were periodically recorded. After 12 h, no **3d** remained. The yields of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ (**6**, 0.0417 mmol, 80%)[5a] and cyclohexene (0.0453 mmol, 87%) were determined by integration of ^{1}H NMR resonances (C_5H_5, =CH vs Ph_3SiCH_3).

Reaction of **3d** *and* PPh_3. A 5 mm NMR tube was charged with **3d** (0.0366 g, 0.0435 mmol),

Ph_3SiCH_3 as a standard (0.0143 g, 0.0521 mmol), and was capped with a septum. The sample was frozen in liquid nitrogen, CD_2Cl_2 (0.8 cm^3) was added, followed by solid PPh_3 (0.0160 g, 0.0610 mmol). The sample was slowly warmed to 0°C, and ^1H and ^{31}P NMR spectra were periodically recorded. After 8 h, no **3d** remained. The yields of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**7**, 0.0413 mmol, 95%),[10] $[Ph_3PC_6H_{11}]^+BF_4^-$ (**8**, 0.0104 mmol, 24%), cyclohexyl fluoride (0.0104 mmol, 24%) and cyclohexene (0.0131 mmol, 30%) were determined by integration of ^1H NMR resonances (C_5H_5, CHX, =CH vs Ph_3SiCH_3). The cyclohexyl fluoride and cyclohexene yields were confirmed by GLC. See text for other data.

Reaction of **3d** *and* PPN^+Br^-. A 5 mm NMR tube was charged with **3d** (0.0244 g, 0.0290 mmol), Ph_3SiCH_3 standard (0.0127 g, 0.0463 mmol), and was capped with a septum. The sample was frozen in liquid nitrogen, CD_2Cl_2 (0.8 cm^3) was added, followed by solid PPN^+Br^- (0.0210 g, 0.0340 mmol). The sample was kept at −40°C for 12 h and then ^1H and ^{31}P NMR spectra were recorded at room temperature. The yields of **7** (0.0287 mmol, 99%) and cyclohexene (0.0281 mmol, 57%) were determined by integration of ^1H NMR resonances (C_5H_5, =CH vs Ph_3SiCH_3). See text for other data.

Preparation of $[Ph_3PC_6H_{11}]^+BF_4^-$ (**8**). A flask was charged with $[Ph_3PC_6H_{11}]^+Br^-$ (0.654 g, 1.54 mmol),[11] $AgBF_4$ (0.352 g, 1.81 mmol), methanol (25 cm^3), and a stir bar. The mixture was stirred for 15 min and was then poured through a 3 cm pad of Celite on a coarse glass frit. The solvent was removed from the filtrate by rotary evaporation. A white microcrystalline powder formed, which was recrystallized from CH_2Cl_2/ether and dried under an oil pump vacuum to give **8** (0.646 g, 1.49 mmol, 94%), m.p. 241°C. IR (cm^{-1}, KBr) ν(BF) 1121 vs, 1054 vs, 996 vs; ^1H NMR (δ, CD_2Cl_2, 25°C) 7.84–7.87 (m, $3C_6H_5$), 3.67 (m, PCH), 2.11 (m, CH_2), 1.83 (m, CH_2), 1.71 (m, CH_2), 1.16 (m, CH_2); $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2) 135.2 (d, J(CP) 2.9 Hz, *p*-Ph), 133.8 (d, J(CP) 9.4 Hz, *m*-Ph), 130.7 (d, J(CP) 12.6 Hz, *o*-Ph), 117.3 (d, J(CP) 83.5 Hz, *i*-Ph), 31.0 (d, J(CP) 46.9 Hz, PCH), 26.8 (d, J(CP) 3.0 Hz, PCCH_2),[20] 26.0 (d, J(CP) 13.8 Hz, PCCCH_2),[20] 25.6 (s, CH_2); $^{31}P\{^1H\}$ (ppm, CD_2Cl_2) 26.7 (s). Found: C, 66.2; H, 6.0. Calc. for $C_{24}H_{28}NF_4P$: C, 66.7; H, 6.1%.

Acknowledgement—We thank the NSF for support of this research.

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