Synthesis and Characterization of Chiral Rhenium σ-Ketone Complexes. Binding Properties of Symmetrical Ketones and Alkylcyclohexanones†

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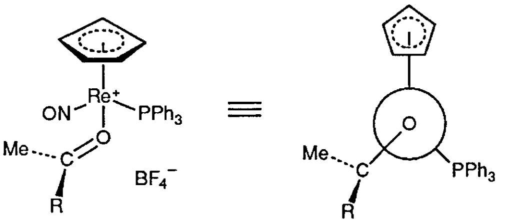
Reactions of the dichloromethane complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(ClCH_2Cl)]BF_4$ **1** with cyclohexanone (**a**), cyclobutanone (**b**), diphenylcyclopropenone (**c**), and tropone (**d**) give the symmetrical σ-ketone complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(\sigma\text{-}O{=}CR_2)]BF_4$ **7a–7d** in 50–85% yields after work-up. Similar reactions of **1** with pentan-3-one (**e**) and 2,4-dimethylpentan-3-one (**f**) give the analogous ketone complexes **7e** and **7f** in good spectroscopic yields, but low isolated yields. However, **7e** can be isolated in 66% yield from the reaction of the chlorobenzene complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(ClC_6H_5)]BF_4$ and pentan-3-one. Reactions of **1** with 3-methylcyclohexanone (**h**) and *trans*-1-decalone (**j**) give complexes **7h** and **7j** as mixtures of Re/C configurational diastereomers (40–71%). Under most conditions, the symmetrical ketone complexes **7a–7e** exhibit a single set of ^1H and ^{13}C NMR resonances for the C=O substituents that are *Z* and *E* to the rhenium. Low-temperature ^1H NMR experiments show that the *Z*/*E* ethyl groups in **7e** exchange with $\Delta G^{\ddagger}_{151\,K} = 7.0$ kcal mol^{-1}.

The synthesis, structure, and reactivity of transition-metal ketone complexes are attracting increasing attention.[1–7] In particular, ketone complexes of chiral metal fragments would seem to have considerable potential in asymmetric organic synthesis. However, there have only been a few studies directed at general methods for the complexation of ketones.[3–7] Thus, structural and functional limitations on ketone ligands are not well defined. Also, few if any chiral metal ketone complexes have been characterized to date.

We recently reported that the racemic and optically active dichloromethane complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(ClCH_2Cl)]BF_4$ **1** reacts with methyl ketones to give racemic and optically active σ complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)\{\sigma\text{-}O{=}C(R)Me\}]BF_4$ (R = Me, **2**; Et, **3**; Pr^i, **4**; Bu^t, **5**; Ph **6**) in high isolated yields, as summarized in Scheme 1.[7] Thus, **1** serves as a functional equivalent of the chiral Lewis acid $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)]^+$ **I**.[8] The methyl ketone ligands in **3–6** adopt conformations in which one ketone face is shielded by the bulky PPh_3 ligand, as shown in **II** (Scheme 1). Consequently, they undergo highly stereoselective hydride reduction. The resulting alkoxide complexes can be readily elaborated to esters of optically active secondary alcohols.[7]



R
2 Me (79%)
3 Et (86%)
4 Pr^i (84%)
5 Bu^t (85%)
6 Ph (85%)

II

Scheme 1 Previously synthesised chiral rhenium ketone complexes

We sought to extend this chemistry by probing the range and scope of ketones that can be ligated to the rhenium fragment **I**. Thus, we set out to systematically define (*a*) ketone complexes that can be efficiently generated in solution, and (*b*) ketone complexes with sufficient thermal stability to be isolated in pure form. In this paper we report (1) high-yield syntheses of a variety of symmetrical σ-ketone complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(\sigma\text{-}O{=}CR_2)]BF_4$ **7**, (2) the preparation of analogous, unsymmetrically substituted alkylcyclohexanone complexes, and (3) spectroscopic and dynamic properties of the preceding compounds.

Results

(1) *Syntheses of Symmetrical Ketone Complexes.*—The dichloromethane complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(ClCH_2Cl)]BF_4$ **1** was generated at −80 °C as described previously.[8] Then the symmetrical cyclic ketones cyclohexanone (**a**), cyclobutanone (**b**), diphenylcyclopropenone (**c**) and tropone (**d**) (cyclohepta-2,4,6-trien-1-one) were added (1.5–5 equivalents). Work-up gave the corresponding σ-ketone complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(\sigma\text{-}O{=}CR_2)]BF_4$ **7a–7d** in 50–85% yields as orange to red powders or crystals, as summarized in Scheme 2.

Complexes **7a–7d** were characterized by microanalyses (Experimental section), and by IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy (Table 1). General features were very similar to those described earlier for the corresponding methyl ketone complexes **2–6**. The σ-ketone binding mode was evident from IR and NMR spectral properties, as discussed below.

Complex **1** and the acyclic ketone pentan-3-one (**e**) were similarly combined. In contrast to the corresponding reaction with acetone reported earlier,[7] work-up gave predominantly the bridging chloride complex $[\{Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)\}_2Cl]BF_4$ **8**.[8] Complex **1** has been previously shown to decompose to **8** when warmed above −20 °C. Apparently, carbon–chlorine bond cleavage of the dichloromethane ligand occurs. Reactions of **1** and weak or sterically encumbered Lewis bases frequently give appreciable quantities of **8**.

The chlorobenzene complex $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(ClC_6H_5)]BF_4$ **9** has recently been shown to be an improved

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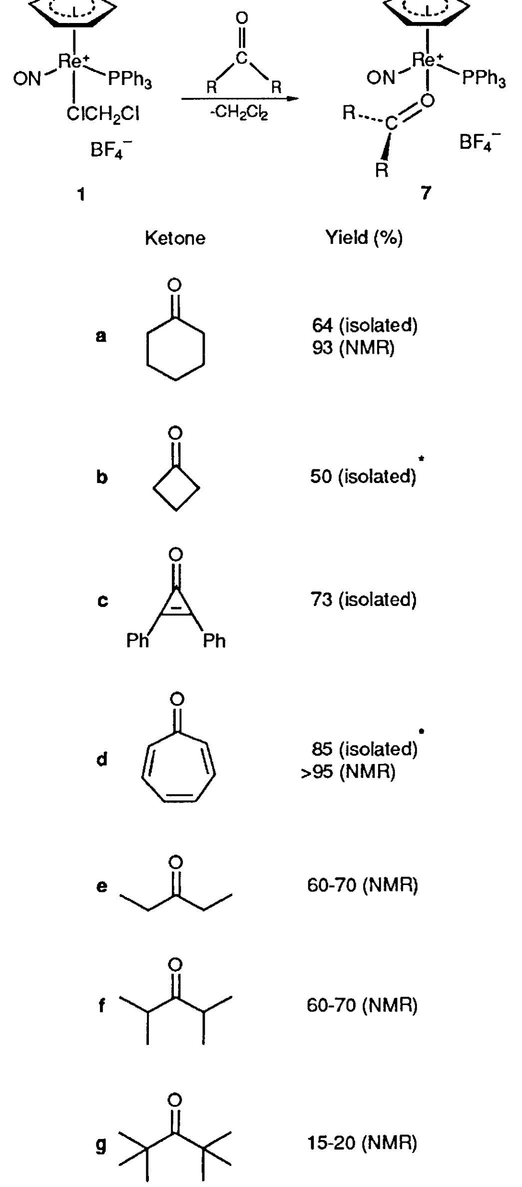
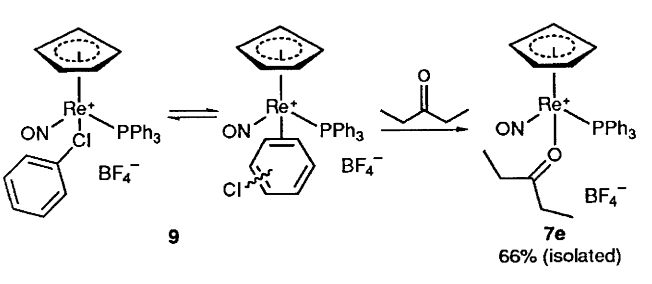
† *Non-SI unit employed:* cal = 4.184 J.



Scheme 2 Preparation of symmetrical ketone complexes $[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CR_2)]BF_4$ **7**. (* Yield following crystallization)



Scheme 3 An alternative route to ketone complexes **7**

functional equivalent of the Lewis acid **I**.[11] Although it exists as a mixture of linkage isomers, it is not subject to irreversible carbon–chlorine bond cleavage below room temperature. Thus, **9** was generated at −42 °C in the presence of pentan-3-one (5 equivalents). Work-up gave the pentan-3-one complex $[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CEt_2)]BF_4$ **7e** in 66% yield, as shown in Scheme 3. Complex **7e** was characterized analogously to **7a**–**7d** (Table 1).

(2) *NMR-monitored Reactions*.—In previous work we observed that adducts of **I** and bulkier ketones such as the pinacolone complex **5** were somewhat more labile than acetone or butan-2-one complexes **2** and **3**.[7] For example, it was not possible to recrystallize **5** from dichloromethane without extensive decomposition. Thus, isolated yields of ketone complexes **7** are potentially poor indicators of yields achieved in solution.[*] Hence, selected reactions of **1** or the similarly generated deuteriodichloromethane complex $[Re(\eta^5-C_5H_5)(NO)(PPh_3)(ClCD_2Cl)]BF_4$ (**1D**) were monitored by low-temperature NMR spectroscopy.

Reactions of **1D** with cyclohexanone or tropone (15 equivalents) gave **7a** or **7d** in 93% to >95% yields over the temperature range of −40 to −15 °C, as assayed by ^{31}P and ^1H NMR spectroscopy (Scheme 2). When the first reaction was repeated with 5 equivalents of cyclohexanone, **7a** formed in 80–90% yields. An analogous reaction of **1** and pentan-3-one (15 equivalents) gave **7e** in 60–70% yields, as assayed by integration of the PPh_3 ^{31}P NMR resonances. This contrasts with the poor preparative result described above. Presumably, **7e** remains in equilibrium with precursor **1**, which would account for the isolation of bridging chloride complex **8** upon work-up.

Surprisingly, reaction of complex **1D** and the more hindered ketone 2,4-dimethylpentan-3-one (**f**) gave the adduct $[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CPr^i_2)BF_4$ **7f** in comparable NMR yields (Scheme 2). Finally, **1D** and the still bulkier ketone 2,2,4,4-tetramethylpentan-3-one (**g**) gave a species with a plausible ^{31}P NMR chemical shift for $[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CBu^t_2)]BF_4$ **7g** in 15–20% yields. The principal product was **8**.

Although detailed rate studies were not conducted, several trends emerged from preliminary experiments. First, the rates of formation of acetone complex **2** and tropone complex **7d** both depended upon ketone concentrations (0.05–0.06 mol dm^{-3}, 4–15 fold excesses of ketones, −36 °C). Under comparable conditions, tropone was significantly more nucleophilic than acetone. However, the rates of formation of acetone, pentan-3-one, and 2,4-dimethylpentan-3-one complexes **2**, **7e** and **7f** only spanned a factor of *ca.* 2 (0.05–0.06 mol dm^{-3}, 15-fold excesses of ketones, −36 °C). Further studies of the mechanisms of these transformations are in progress.[12]

(3) *Syntheses of Alkylcyclohexanone Complexes*.—Reactions of complex **1** and some unsymmetrically substituted alkylcyclohexanones were studied next. First, in a preparative reaction, **1** was treated with 3-methylcyclohexanone (**h**; 3 equivalents) at −80 °C. Work-up gave the adduct $[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CCH_2CH_2CH_2CH(Me)CH_2)]BF_4$ **7h** in 71% yield, as shown in Scheme 4. In contrast to complexes **7a**–**7g** an asymmetric carbon is present in the ketone ligand in **7h**. Accordingly, NMR spectra (Table 1) indicated a (50 ± 3):(50 ± 3) mixture of isomers. These were assigned as Re/C configurational diastereomers, as opposed to C=O geometric (*E*/*Z*) isomers, on the basis of data described below.

Several preparative and NMR-monitored reactions of complex **1** and 2-methylcyclohexanone (**i**) were conducted. Numerous products formed, and in no case was any species with a plausible ^{31}P NMR chemical shift for the expected adduct $[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CCH_2CH_2CH_2CH_2CHMe)]BF_4$ **7i** present in greater than *ca.* 25% yield.

We sought to study analogous reactions of a slightly less

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[*] It should be emphasized that work-up options for isolating complexes **2**–**7** are severely restricted. The complexes are insoluble in ether and hydrocarbon solvents. They are soluble in chlorocarbons, but prolonged chromatography or crystallizations can be accompanied by decomposition (*e.g.* **8**). Complexes **2**–**7** are soluble in more polar media such as acetonitrile or dimethyl sulphoxide, but the ketone ligands are very rapidly displaced.

bulky 2-alkylcyclohexanone. Thus, complex **1** was treated with *trans*-1-decalone [octahydro-2*H*-naphthalen-1-one] (**j**, 5 equivalents) at −80 °C. Work-up gave the adduct $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)\{\sigma\text{-}O{=}CCH_2CH_2CH_2CH(CH_2)CH(CH_2CH_2CH_2)\}]BF_4$ **7j** in 40% yield (Scheme 4). NMR analysis indicated a (47 ± 2):(53 ± 2) mixture of diastereomers. A control experiment with a mixture of *cis*- and *trans*-1-decalone showed that no isomerization of the ring fusion had occurred in **7j**. Thus, the isomers were assigned as Re/C configurational diastereomers, analogous to those obtained with **7h**.

(4) *Dynamic NMR Experiments.*—In ketone complexes **7** one carbonyl carbon substituent bears a *Z* (*cis*) relationship to the rhenium, and the other bears an *E* (*trans*) relationship. However, as outlined in Table 1, symmetrical ketone complexes **7a**–**7e** give only one set of ^1H and ^{13}C NMR resonances for the *Z* and *E* substituents. Earlier studies have established that the

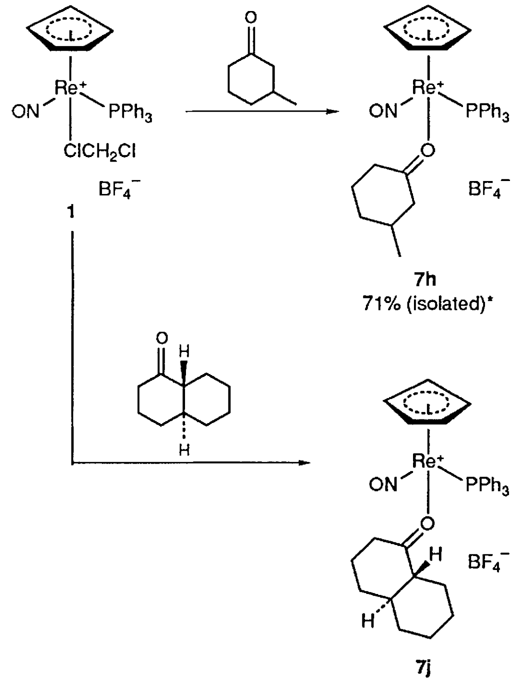
Table 1 Spectroscopic characterization of new isolable ketone complexes

Complex	IR (cm^{-1}, KBr)	^1H NMR^a (δ)	^{13}C-{^1H} NMR^b (δ)	^{31}P-{^1H} NMR^c (δ)
7a	ν(NO) 1687vs ν(C=O) 1619m	7.60–7.25 (m, $3C_6H_5$) 5.59 (s, C_5H_5) 2.66–1.55 (m, 10 H)	236.2 (d, *J* = 1.9, CO), 133.7 (d, *J* = 10.9, *o*-C of PPh_3) 131.9 (d, *J* = 2.4, *p*-C of PPh_3) 131.8 (d, *J* = 55.3, *i*-C of PPh_3) 129.6 (d, *J* = 10.8, *m*-C of PPh_3) 92.9 (d, *J* = 1.4, C_5H_5) 42.4 (s, $2CH_2$) 26.3 (s, $2CH_2$) 23.7 (s, CH_2)	18.5 (s)
7b	ν(NO) 1706vs ν(C=O) 1669s	7.65–7.30 (m, $3C_6H_5$) 5.63 (s, C_5H_5) 3.40–3.30 (m, 2 H) 3.15–3.00 (m, 2 H) 1.90 (m, 2 H)	133.9 (d, *J* = 11.0, *o*-C of PPh_3), 132.1 (d, *J* = 2.4, *p*-C of PPh_3), 131.4 (d, *J* = 55.9, *i*-C of PPh_3), 129.6 (d, *J* = 10.8, *m*-C of PPh_3), 93.1 (s, C_5H_5) 47.3 (s, $2CH_2$) 10.1 (s, CH_2)^d	18.4 (s)
7c	ν(NO) 1675vs ν(C=O) 1543s ν(C=C) 1858s	8.02–7.35 (m, $5C_6H_5$) 5.62 (s, C_5H_5)	165.9 (d, *J* = 3.2, CO) 146.3 (s, 2*C*Ph) 133.9 (d, *J* = 10.9, *o*-C of PPh_3) 132.1 (d, *J* = 54.8, *i*-C of PPh_3) 131.6 (d, *J* = 2.2, *p*-C of PPh_3) 129.4 (d, *J* = 10.7, *m*-C of PPh_3) 135.5 (s, *p*-C of CPh) 133.3 (s, *o*-C of CPh) 130.2 (s, *m*-C of CPh) 121.1 (s, *i*-C of CPh)^e 92.1 (d, *J* = 1.2, C_5H_5)	19.8 (s)
7d	ν(NO) 1669vs ν(C=O) 1507s	7.65–7.30 (m, 21 H) 5.56 (s, C_5H_5)	193.1 (s, CO) 141.7 (s, 2CH) 141.6 (s, 2CH) 139.8 (s, 2CH) 133.6 (d, *J* = 10.8, *o*-C of PPh_3) 131.73 (d, *J* = 54.9, *i*-C of PPh_3) 131.66 (d, *J* = 2.3, *p*-C of PPh_3) 129.4 (d, *J* = 10.7, *m*-C of PPh_3) 92.6 (d, *J* = 1.3, C_5H_5)	18.4(s)
7e	ν(NO) 1677vs ν(C=O) 1601s	7.59–7.29 (m, $3C_6H_5$) 5.60 (s, C_5H_5) 2.84 (dq, *J* = 7.2, 18.2, 2 H) 2.46 (dq, *J* = 7.4, 18.5, 2 H) 0.94 (t, *J* = 7.3, $2CH_3$)	238.1 (s, CO) 133.9 (d, *J* = 11.0, *o*-C of PPh_3) 132.1 (s, *p*-C of PPh_3) 131.9 (d, *J* = 55.3, *i*-C of PPh_3) 129.7 (d, *J* = 10.7, *m*-C of PPh_3) 93.0 (s, C_5H_5) 37.5 (s, $2CH_3$) 8.5 (s, $2CH_2$)	18.9 (s)
7h^f	ν(NO) 1686vs ν(C=O) 1612s	7.61–7.29 (m, $3C_6H_5$) 5.60 (s, C_5H_5) 2.68–0.95 (m) 0.96/0.95 (d, *J* = 6.5, CH_3)	236.1 (s, CO) 133.9 (d, *J* = 10.8, *o*-C of PPh_3) 132.1 (d, *J* = 2.3, *p*-C of PPh_3) 132.0 (d, *J* = 55.3, *i*-C of PPh_3) 129.7 (d, *J* = 10.8, *m*-C of PPh_3) 93.0 (s, C_5H_5) 50.2/50.0 (s, CH_2) 41.8/41.6 (s, CH_2) 34.4/34.2 (s, CH_2) 32.2 (s, CH) 25.3/25.2 (s, CH_2) 21.8/21.7 (s, CH_3)	18.45/18.40 (s)

Table 1 (*continued*)

Complex	IR (cm^{-1}, KBr)	^{1}H NMR[a] (δ)	^{13}C-{^{1}H} NMR[b] (δ)	^{31}P-{^{1}H} NMR[c] (δ)
7j[f]	ν(NO) 1686vs ν(C=O) 1608s	7.62–7.24 (m, 3C_6H_5) 5.62/5.56 (s, C_5H_5) 2.82–0.84 (m, 16 H)	239.3/236.9 (s, CO) 134.03/133.97 (d, *J* = 10.9, *o*-C of PPh_3) 132.2/132.0 (s, *p*-C of PPh_3) 131.5 (d, *J* = 47.9, *i*-C of PPh_3)[g] 129.81/129.76 (d, *J* = 10.9, *m*-C of PPh_3) 57.7/56.7 (s, CH) 46.6/45.6 (s, CH) 34.2/33.9 (s, CH_2) 32.25/32.17 (s, CH_2) 27.0/26.9 (s, CH_2) 25.6/25.5 (s, CH_2) 25.40/25.35 (s, CH_2) 25.22/25.15 (s, CH_2)	20.1/19.6 (s)

[a] At 300 MHz and ambient probe temperature in CD_2Cl_2 and referenced to internal $SiMe_4$; all couplings (Hz) are to hydrogen unless noted. [b] At 75 MHz and ambient probe temperature in CD_2Cl_2 and referenced to internal $SiMe_4$; all couplings are to phosphorus unless noted. Assignments of PPh_3 carbon resonances were made as described in footnote *c* of Table 1 in ref. 9. [c] At 121 MHz and ambient probe temperature in CD_2Cl_2 and referenced to external 85% H_3PO_4. [d] The CO resonance was not observed. [e] Assignments made by analogy to those established for the free ligand[10] [f] Mixture of Re/C configurational diastereomers; most NMR resonances doubled. [g] One *ipso*-carbon resonance not observed.



Scheme 4 Synthesis of alkylcyclohexanone complexes. (* Mixture of Re/C diastereomers)

acetone ligand in **2** exchanges only slowly with [$^2H_6$]acetone at room temperature. Thus, there must be an intramolecular pathway for rendering the *Z* and *E* substituents equivalent.

Hence, low-temperature 300 MHz ^{1}H NMR spectra of the pentan-3-one complex **7e** were recorded in $CDFCl_2$. This solvent remains liquid at temperatures as low as −150 °C.[13] As shown in Fig. 1, the single methyl resonance decoalesced into separate *Z* and *E* methyl resonances of equal intensity (δ 1.166 and 0.850; Δν 95 Hz). Application of the coalescence formula[14] gave a $\Delta G^{\ddagger}_{151\,\mathrm{K}}$ of only 7.0 ± 0.1 kcal mol^{-1} for the process that exchanges the methyl groups. Thus, under the NMR conditions used in Table 1, *Z*/*E* C=O geometric isomers of unsymmetrical ketone complexes **7h** and **7j** should not be observable.

Discussion

(1) *Spectroscopic Properties of Ketone Complexes.*—As would be intuitively expected, the IR ν(C=O) of σ-ketone complexes **7a**–**7e**, **7h** and **7j** (Table 1) are lowered by 85–130 cm^{-1} relative to those of the corresponding free ketones. Comparisons for five complexes are given in Table 2. Interestingly, most samples of cyclohexanone complex **7a** exhibited two closely spaced sets of IR ν(C=O) and ν(NO) in KBr. Such 'solid-state splitting' is common, and might be due to two conformations of the ketone ligand. This phenomenon was not observed in IR spectra recorded in dichloromethane.

Similarly, saturated ketones exhibit a *ca.* 25 ppm downfield shift of the C=O ^{13}C NMR resonance upon co-ordination to the rhenium fragment **I**. Data are summarized in Table 2. Comparable downfield ^{13}C NMR shifts are also observed in

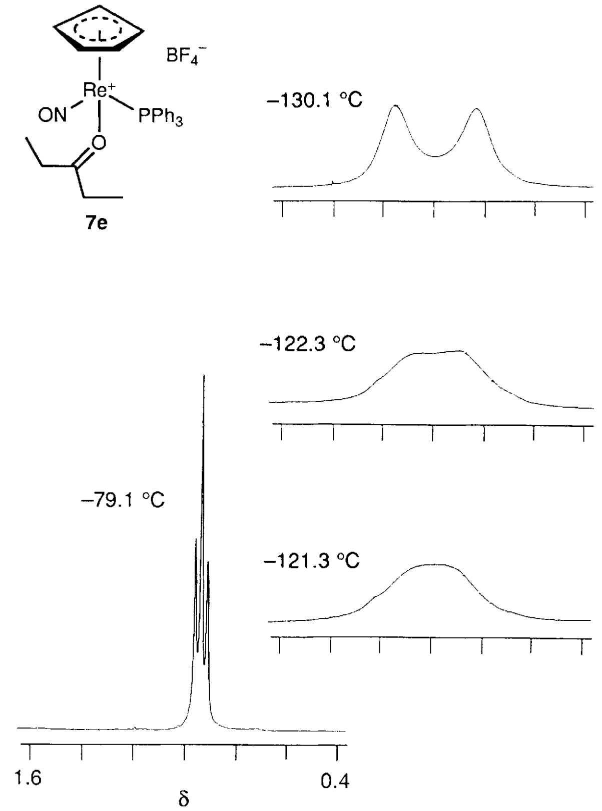
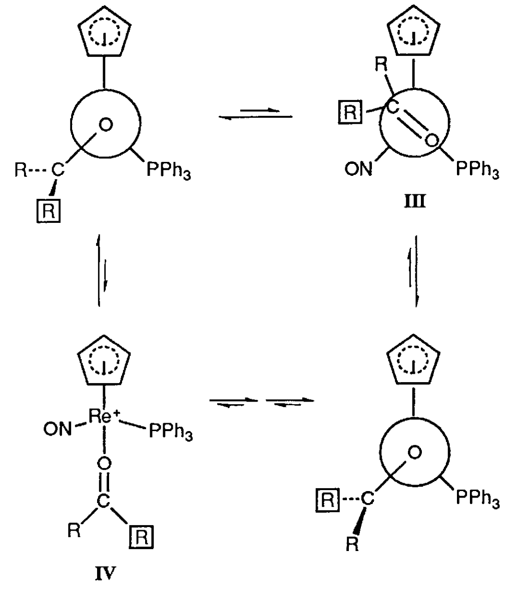


Fig. 1 Variable-temperature ^{1}H NMR spectra of pentan-3-one complex **7e** in $CDFCl_2$

Table 2 Comparison of spectroscopic properties of free ketones and the ketone ligands in $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(\sigma\text{-}O{=}CR_2)]BF_4$ **7**

	IR ν(C=O)/cm^{-1}			^{13}C NMR (C=O, δ, CH_2Cl_2)		
Ketone	Unco-ordinated[a]	Co-ordinated[b]	Δ	Unco-ordinated	Co-ordinated	Δ
a Cyclohexanone	1711	1619	92	211.4	236.2	24.8
b Cyclobutanone	1789	1669	120	215.3	*c*	—
c Diphenylcyclopropenone	1629	1543	86	155.6	165.9	10.3
d Tropone	1634	1507	127	188.0	193.1	5.1
e Pentan-3-one	1722	1601	121	211.9	238.1	26.2

[a] In CH_2Cl_2. [b] In KBr. [c] Not observed.



Scheme 5 Possible mechanisms for the intramolecular exchange of *E* and *Z* alkyl groups in symmetrical ketone complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(\sigma\text{-}O{=}CR_2)]BF_4$ **7**

complexes of **I** with alkyl halides (RCH_2X)[15] and nitriles (RCN).[16] {Range of RC≡N ^{13}C NMR chemical shifts for three $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(NCR)]X$ complexes ($CDCl_3$): 140.4–145.0 ppm}. In each of these cases, the carbon is β to the rhenium and separated by a heteroatom. However, the unsaturated ketone ligands diphenylcyclopropanone (**c**) and tropone (**d**) show smaller changes in chemical shifts (Table 2). A dipolar, aromatic resonance form makes a considerable contribution to the ground states of these compounds. Thus, they differ electronically from the other ketone ligands.

We have recently shown that complex **1** reacts with 1,3-dichloroacetone and 1,3-difluoroacetone to give the π-ketone complexes $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)\{\eta^2\text{-}O{=}C(CH_2X)_2\}]BF_4$.[17] Such linkage isomers are readily distinguished from σ complexes **7** on the basis of the C=O ^{13}C NMR resonance, which shifts upfield to 77–84, and the PPh_3 ^{31}P NMR resonance which shifts upfield to δ 9–10. Also, IR ν(C=O) are no longer observed, and the IR ν(NO) increase to 1740–1762 cm^{-1}. Note that α-halogenoketones are weaker σ donors and stronger π acceptors than aliphatic ketones. As elaborated elsewhere, this accounts for the change in ground-state binding mode and the IR ν(NO) trend.[17,18]

(2) *Dynamic NMR Properties.*—As noted above, the ^{1}H NMR spectra in Fig. 1 establish a facile intramolecular mechanism for exchange of the *Z*/*E* ethyl groups in pentan-3-one complex **7e** ($\Delta G^\ddagger_{151K}$ 7.0 kcal mol^{-1}). Acetone complex **2** undergoes similarly facile methyl group exchange ($\Delta G^\ddagger_{133K}$ 6.0 kcal mol^{-1}), as shown by low-temperature ^{13}C NMR studies.[7c] We have previously considered the possibility of two exchange pathways, which are sketched in abridged form in Scheme 5. The first involves an intemediate π-ketone complex **III**. The second features a linear σ complex **IV**. Several variants of the latter pathway are possible.[7c]

The rhenium fragment **I** forms π complexes of idealized geometry **III** with 1,3-difluoroacetone and aliphatic aldehydes.[17,19] With fluoroacetone and most aromatic aldehydes, mixtures of π and σ complexes are observed.[17,18] Thus, the π and σ binding modes can be close in energy. However, π isomers of ketone complexes **2**–**7** bring *both* C=O alkyl substituents into close proximity of rhenium ligands. Hence, steric interactions should be pronounced. However, there is only a *ca.* 1 kcal mol^{-1} difference in activation energies between methyl-group exchange in **2** and ethyl-group exchange in **7e**. We suggest that this is too small to be consistent with a π intermediate, and that the data are best modelled by a mechanism involving a linear σ complex.

Barriers to *Z*/*E* C=O substituent exchange in ketone/Lewis acid adducts are of fundamental interest. However, data are extremely scarce. Experiments by Courtot and co-workers[20] give a $\Delta G^\ddagger_{199K}$ of *ca.* 9.6 kcal mol^{-1} for intramolecular *Z*/*E* methyl-group exchange in the platinum acetone complex *trans*-$[PtCl_2(py)(\sigma\text{-}O{=}CMe_2)]$ (py = pyridine). Similarly, intramolecular ethyl-group exchange in the pentan-3-one complex $F_3B\text{–}O{=}CEt_2$ occurs with a $\Delta G^\ddagger_{172K}$ of 8.3 kcal mol^{-1} [equation (1)].[21] Thus, based upon these limited data, low *Z*/*E* exchange barriers appear to be general.

(1)

(3) *Scope of Syntheses.*—The preceding data establish that complexes of the chiral Lewis acid **I** and all but very hindered ketones can be generated in good to quantitative spectroscopic yields from the dichloromethane complex **1**. Further yield optimization can likely be achieved by use of the chlorobenzene complex **9**. Hence, there is considerable potential for the development of general synthetic methodology involving ketone complexes of the formulae **2**–**7**.

The σ-binding mode dominates for all but certain polyfluorinated and polychlorinated ketone complexes of **I**.[17] Thus, linkage isomers are observed only in rare cases. However, chiral ketones can form two diastereomeric adducts. Our initial results with alkylcyclohexanones do not show a high degree of chiral recognition in the binding event.

Only a few other complexes of ketones **a**–**j** have been reported in the literature. For example, Rosenblum and Schmidt and co-workers[3,4] have characterized iron cyclohexanone and 2,4-dimethylpentan-3-one complexes of the formula $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(\sigma\text{-}O{=}CR_2)]X$. The former exhibits a ν(C=O) (1610 cm^{-1}) that is very close to that of rhenium analogue **7a**. Boudjouk *et al.*[22] have reported the synthesis of analogous iron diphenylcyclopropenone and tropone complexes, and have determined the crystal structure of the latter. These also exhibit ν(C=O) (1555, 1508 cm^{-1}) that are close to those of rhenium analogues **7c** and **7d** (Tables 1 and 2). Co-ordination compounds of diphenylcyclopropenone and tropone have also been prepared.[23] A rhodium diphenylcyclopropenone complex has been recently described by Stang and co-workers[24]

Future reports will describe the extension of the reactions in Schemes 2 and 3 to esters[25] and simple α,β-unsaturated ketones. A rich ligand-based chemistry can be anticipated for ketone complexes **2**–**7** and related adducts of the chiral fragment **I**.

Experimental

General Data.—Instrumentation, general procedures, and solvent purifications were identical to those described in a previous paper.[7c] Cyclohexanone, pentan-3-one, and alkyl-substituted derivatives (Aldrich) were distilled from $CaSO_4$. Cyclobutanone, diphenylcyclopropenone, *trans*-1-decalone (Aldrich), and tropone (Lancaster) were used as received. Melting points were determined in evacuated capillaries using a calibrated thermometer.[26]

Preparations.—$[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CCH_2CH_2CH_2CH_2CH_2)]BF_4$ **7a**. A Schlenk flask was charged with $[Re(\eta^5-C_5H_5)(NO)(PPh_3)(Me)]$ **10** (336 mg, 0.601 mmol),[27] CH_2Cl_2 (3 cm^3), and a stir bar, and was cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (0.062 cm^3, 0.626 mmol) and cyclohexanone (0.311 cm^3, 3.00 mmol) were sequentially added with stirring. The solution was allowed to warm slowly to room temperature, and was then transferred *via* cannula to a flask of rapidly stirred diethyl ether. An orange powder precipitated, which was collected by filtration and dissolved in the minimum amount of CH_2Cl_2. The solution was again transferred to a flask of rapidly stirred ether. The orange powder which formed was collected and dried under vacuum to give complex **7a** (282 mg, 0.387 mmol, 64%), m.p. 163–166 °C (decomp.) (Found: C, 47.90; H, 4.20. Calc. for $C_{29}H_{30}BF_4NO_2PRe$: C, 47.80; H, 4.15%).

$[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CCH_2CH_2CH_2)]BF_4$ **7b**. Complex **10** (115 mg, 0.206 mmol), $HBF_4{\cdot}OEt_2$ (0.032 cm^3, 0.216 mmol), and cyclobutanone (0.031 cm^3, 0.415 mmol) were combined in a procedure similar to that given for complex **7a**. An identical work-up gave an orange powder, which was dissolved in the minimum of CH_2Cl_2. Ether was slowly added by vapour diffusion. Red-orange crystals formed, which were collected by filtration and dried under vacuum to give complex **7b** (72 mg, 0.103 mmol, 50%), m.p. 150–154 °C (decomp.) (Found: C, 46.15; H, 3.85. Calc. for $C_{27}H_{26}BF_4NO_2PRe$: C, 46.30; H, 3.75%).

$[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CCPh{=}CPh)]BF_4$ **7c**. Complex **10** (123 mg, 0.220 mmol), $HBF_4{\cdot}OEt_2$ (0.034 cm^3, 0.231 mmol) and diphenylcyclopropenone (68 mg, 0.330 mmol) were combined in a procedure similar to that given for complex **7a**. An identical work-up gave a waxy orange solid, which was collected by filtration and dried under vacuum to give complex **7c** (135 mg, 0.161 mmol, 73%), m.p. 166–172 °C (decomp.) (Found: C, 54.45; H, 3.75. Calc. for $C_{38}H_{30}BF_4NO_2PRe$: C, 54.55; H, 3.60%).

$[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CCH{=}CHCH{=}CHCH{=}CH)]\ BF_4$ **7d**. Complex **10** (115 mg, 0.206 mmol), $HBF_4{\cdot}OEt_2$ (0.032 cm^3, 0.216 mmol), and tropone (0.038 cm^3, 0.392 mmol) were combined in a procedure similar to that given for complex **7a**. An identical work-up gave a red powder, which was dissolved in the minimum of CH_2Cl_2. Ether was slowly added by vapour diffusion. Dark red needles formed, which were collected by filtration and dried under vacuum to give complex **7d** (130 mg, 0.176 mmol, 85%), m.p. 176–178 °C (decomp.) (Found: C, 49.15; H, 3.45. Calc. for $C_{30}H_{26}BF_4NO_2PRe$: C, 48.90; H, 3.55%).

$[Re(\eta^5-C_5H_5)(NO)(PPh_3)(\sigma-O{=}CEt_2)]BF_4$ **7e**. A Schlenk flask was charged with complex **10** (173 mg, 0.310 mmol), pentan-3-one (0.160 cm^3, 1.51 mmol), C_6H_5Cl (1.7 cm^3), and a stir bar, and was cooled in a C_6H_5Cl–CO_2 bath (−42 °C). Then $HBF_4{\cdot}OEt_2$ (0.041 cm^3, 0.328 mmol) was added with stirring. The solution was allowed to warm slowly to room temperature and then frozen solid with a liquid-nitrogen bath. Ether (6 cm^3) was layered onto the solid. This mixture was allowed to warm slowly to room temperature, with stirring subsequent to liquefaction. A yellow-orange powder precipitated, which was collected by filtration and dried under vacuum to give complex **7e** (146 mg, 0.204 mmol, 66%), m.p. 119–122 °C (decomp.) (Found: C, 46.80; H, 4.35. Calc. for $C_{28}H_{30}BF_4NO_2PRe$: C, 46.95; H, 4.20%).

$[Re(\eta^5-C_5H_5)(NO)(PPh_3)\{\sigma-O{=}CCH_2CH_2CH_2CH(Me)CH_2\}]BF_4$ **7h**. Complex **10** (108 mg, 0.193 mmol), $HBF_4{\cdot}OEt_2$ (0.030 cm^3, 0.203 mmol), and 3-methylcyclohexanone (0.071 cm^3, 0.580 mmol) were combined in a procedure similar to that given for complex **7a**. An identical work-up gave an orange-red oil, which was dissolved in the minimum of CH_2Cl_2. Ether was slowly added *via* vapour diffusion. Red polymorphous crystals formed, which were collected by filtration and dried under vacuum to give complex **7h** (102 mg, 0.137 mmol, 71%), m.p. 157–161 °C (decomp.) (Found: C, 48.50; H, 4.35. Calc. for $C_{30}H_{22}BF_4NO_2PRe$: C, 48.50; H, 4.35%).

$[Re(\eta^5-C_5H_5)(NO)(PPh_3)\{\sigma-O{=}CCH_2CH_2CH_2CH(CH_2)CH(CH_2CH_2CH_2)\}]BF_4$ **7j**. Complex **10** (206 mg, 0.369 mmol), $HBF_4{\cdot}OEt_2$ (0.038 cm^3, 0.387 mmol), and *trans*-1-decalone (294 mg, 1.93 mmol) were combined in a procedure similar to that given for **7a**. The solution was allowed to warm slowly to room temperature, and was then transferred *via* cannula to a flask of rapidly stirred ether. An orange powder formed, which was collected by filtration and dried under vacuum to give complex **7j** (115 mg, 0.147 mmol, 40%), m.p. 132–135 °C (decomp.) (Found: C, 50.50; H, 5.00. Calc. for $C_{33}H_{36}BF_4NO_2PRe$: C, 50.65; H, 4.65%).

Generation of Other Ketone Complexes.—Compounds that were too labile to isolate were characterized by NMR spectroscopy. The following procedure is representative. A 5 mm NMR tube was charged with complex **10** (32 mg, 0.057 mmol) and CD_2Cl_2 (0.7 cm^3) under argon, and was capped with a septum. The tube was cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (0.008 cm^3, 0.061 mmol) and 2,4-dimethylpentan-3-one (0.120 cm^3, 0.847 mmol) were sequentially added. The sample was allowed to warm slowly to room temperature and NMR spectra were recorded. NMR data: **7f**, ^1H, δ 5.61 (s, C_5H_5); ^{31}P, δ 17.9 (s); **7g**, ^1H, δ 5.41 (s, C_5H_5); ^{31}P, δ 19.7 (s).

Dynamic NMR Experiments.—Low-temperature NMR experiments were conducted as described previously.[28] Probe temperatures were calibrated with methanol and were assumed to be accurate to ±1 °C. Rate constants and $\Delta G^{\ddagger}$ were calculated by standard methods.[14]

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