Anhydrous Monomeric Glyoxal: Pyrolytic Generation and Stabilization by the Chiral Rhenium Fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$

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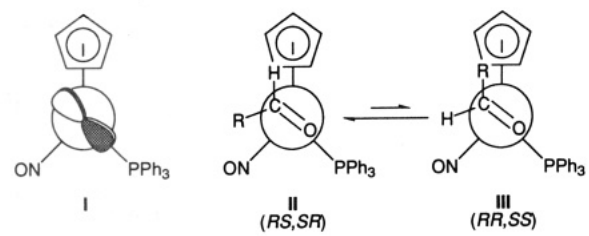
Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ ($\mathbf{5}^+BF_4^-$) and a CH_3OH/H_2O glyoxal solution gives the π complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHCH{=}O)]^+BF_4^-$ ($\mathbf{1}^+BF_4^-$) in 17% yield as a 95:5 mixture of *RS,SR*/*RR,SS* diastereomers. The trimeric dihydrate of glyoxal and P_2O_5 are pyrolyzed under vacuum at 160 °C. Pure anhydrous monomeric glyoxal can be trapped at −80 °C, as assayed by ^1H and ^{13}C NMR. Subsequent reaction with $\mathbf{5}^+BF_4^-$ gives $\mathbf{1}^+BF_4^-$ (33%; 95:5 *RS,SR*/*RR,SS*). The NMR and IR properties of $\mathbf{1}^+BF_4^-$ are studied in detail, especially with regard to the free and bound O=CH moieties. A ^1H NOE experiment suggests that an *s-cis* O=C—C=O conformer dominates in solution. The crystal structure of (*RS,SR*)-$\mathbf{1}^+BF_4^-$ also shows an *s-cis* conformer, with free/bound O=C bond lengths of 1.206(7)/1.331(5) Å. Reaction of $\mathbf{1}^+BF_4^-$ and NaI in CH_3CN gives $\mathbf{1}^+I^-$ (75%), which when placed in CH_3OH gives $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (69%). Reaction of $\mathbf{1}^+BF_4^-$ and CD_3CN at 80 °C gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCD_3)]^+BF_4^-$. However, in none of these substitutions is free glyoxal detected. Well-defined additions to the glyoxal ligand could not be effected.

Although α-dicarbonyl compounds, O=C(R)—(R′)-C=O, are of considerable utility in organic synthesis, many readily add water across one O=C bond to give hydrates. In particular, the parent member, dialdehyde glyoxal (O=CH—CH=O), is commercially available only as a solid trimeric dihydrate, or aqueous solutions that contain mixtures of monomeric, dimeric, and trimeric hydrates.[1] Anhydrous monomeric glyoxal has been generated in the gas phase by copyrolysis of the trimeric dihydrate and P_2O_5[2] and persists at least to some extent in condensed phases at low temperatures.[2b,c] Such preparations have not to our knowledge been employed in synthesis. In contrast, numerous applications of hydrated glyoxal have been developed.[1a,3] However, a convenient means of generating this versatile two-carbon synthon in nonaqueous, aprotic media would greatly extend its utility.

Reactive organic molecules are often stabilized by complexation to transition metal fragments. In this context, we have conducted an extensive study of π aldehyde complexes of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**).[4–8] These can be prepared in high yields from substitution-labile chlorohydrocarbon complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClR)]^+BF_4^-$. The aldehyde ligands adopt Re—(O=C) conformations that (1) allow high degrees of overlap of their π^* acceptor orbitals and the rhenium fragment d-orbital HOMO depicted in Scheme 1 and (2) direct the larger =CHR terminus *anti* to the bulky PPh_3 ligand. Within these boundary conditions, two configurational diastereomers are possible, as illustrated by **II** (*RS,SR*) and **III** (*RR,SS*) in Scheme 1. These differ in the O=C enantioface bound to rhenium, and the latter is destabilized due to steric interactions between the O=CH***R*** substituent and the cyclopentadienyl ligand. Equilibrium ratios are ≥99:1 for aliphatic aldehydes and acrolein, and (98–74):(2–26) for aromatic aldehydes, depending upon aryl substituents and conditions.[6,8]

Scheme 1. (I) d-Orbital HOMO of the Pyramidal 16-Valence-Electron Rhenium Fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ and (II, III) Idealized Structures of Diastereomeric Aldehyde Complexes of I



We sought to extend the preceding chemistry to α-dicarbonyl compounds that are normally difficult to access in aprotic media. We targeted as an initial objective the π glyoxal complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CH\text{-}$

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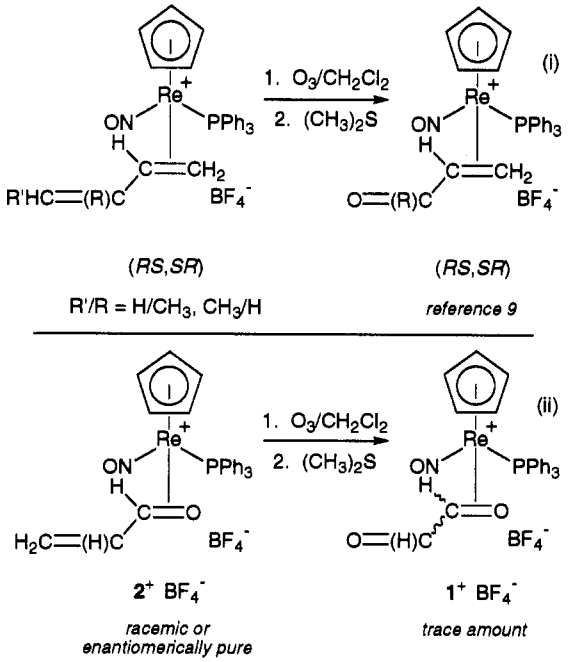
Scheme 2. Ozonolysis Reactions



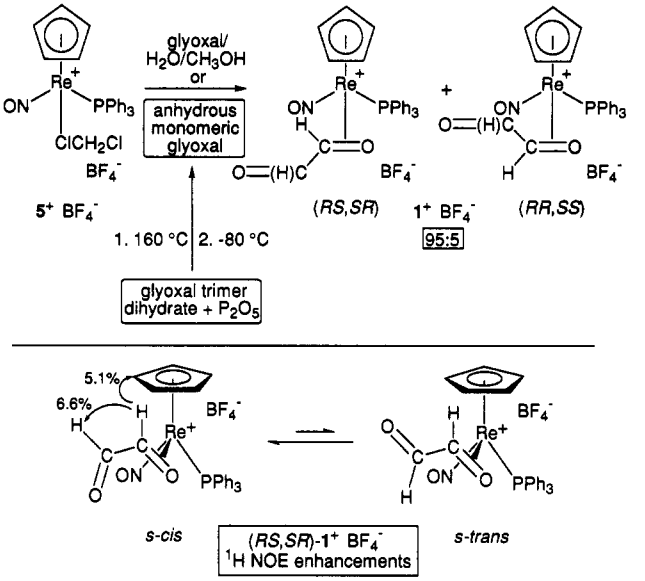
CH=O)]$^+BF_4^-$ (1^+ BF_4^-) and describe the synthesis, structure, and reactivity of this compound below.

Results

1. Syntheses of a Glyoxal Complex. In view of the frequent incompatibility of aqueous solutions and organometallic compounds, syntheses that did not require commercial glyoxal were investigated first. Previously, η^2-diene complexes of the rhenium fragment I have been cleanly ozonolyzed to the corresponding C=C-ligated enone or enal complexes, as exemplified in Scheme 2, eq i.[9] Hence, the O=C-ligated π acrolein complex [(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-O=CHCH=CH_2)]$^+BF_4^-$ ($2^+BF_4^-$)[8] was suspended in dichloromethane and analogously treated with ozone and then dimethyl sulfide (Scheme 2, eq ii). Reactions were also conducted with the more soluble enantiomerically pure complex (−)-(*SR*)-$2^+BF_4^-$, which allowed homogeneous conditions, as well as varying amounts of ozone and dimethyl sulfide. However, ^1H and ^{31}P NMR spectra of the crude reaction mixtures showed only trace amounts (up to 5%) of the target complex $1^+BF_4^-$. The major product was triphenylphosphine oxide. Nonetheless, we were encouraged by the apparent stability of $1^+BF_4^-$ and turned to other synthetic approaches.

Preparations involving aqueous glyoxal were studied next. As a test case, the synthesis of the previously characterized formaldehyde complex [(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-O=CH_2)]$^+BF_4^-$ ($3^+BF_4^-$)[10] from aqueous formaldehyde was attempted first. Thus, the methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**4**), $MgSO_4$ drying agent, CH_2Cl_2, and HBF_4·OEt_2 were combined at −80 °C. This recipe has been shown to generate, at least in the absence of $MgSO_4$, the substitution-labile dichloromethane complex [(η^5-C_5H_5)Re(NO)(PPh_3)($ClCH_2Cl$)]$^+BF_4^-$ ($5^+BF_4^-$).[11] Aqueous formaldehyde was added, giving a single liquid phase. Workup afforded $3^+BF_4^-$ in 54% yield. In the absence of $MgSO_4$, $3^+BF_4^-$ was isolated in only 8% yield.

Scheme 3. Syntheses and Possible Solution Conformations of Glyoxal Complex $1^+BF_4^-$



An analogous reaction was conducted with aqueous glyoxal. However, none of the target complex $1^+BF_4^-$ was detected. Thus, conditions were varied empirically. First, a similar reaction was conducted with *methanolic* aqueous glyoxal. Workup gave $1^+BF_4^-$ in 13% yield. Second, a reaction with methanolic aqueous glyoxal was conducted *without* $MgSO_4$ (Scheme 3). Workup gave high yields of a crude product that contained 49–57% $1^+BF_4^-$, as assayed by ^1H NMR. However, purification proved difficult, and $1^+BF_4^-$ could only be isolated in 17% yield.

Hence, a third synthetic approach was investigated. First, the trimeric dihydrate of glyoxal and P_2O_5 were heated at 160 °C under vacuum, and the volatiles were trapped at −80 °C.[2] The resulting light yellow-green solid turned white if kept for extended periods. Importantly, free glyoxal has a visible absorption at 420 nm (30–93 K).[12] A fresh sample was dissolved in $CDCl_3$, and ^1H and ^{13}C NMR spectra were recorded. Each showed a single resonance in the range that would be expected for free glyoxal (δ 9.30, 188.2 ppm). No other species were detected. Stock solutions were prepared by dissolving fresh samples in measured amounts of CH_2Cl_2 or THF. Titers were established by dissolving aliquots in $CDCl_3$ and integrating the glyoxal and solvent ^1H resonances. THF solutions showed visible absorptions at 416 nm (−80 °C) and 426 nm (ambient temperature, ϵ ca. 9.5 M^{-1} cm^{-1}).

On the basis of the preceding NMR and visible spectra, we conclude that the above procedure affords anhydrous monomeric glyoxal of high purity. To our knowledge, no other NMR data are available for this compound. Next, the dichloromethane complex $5^+BF_4^-$ and a dichloromethane solution of glyoxal (ca. 8 equiv) were combined at −80 °C. An analogous reaction was conducted with the corresponding chlorobenzene complex (−45 °C).[13] In both

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cases, workups gave $1^+BF_4^-$ as a tan powder in 33% yield. Considerable quantities of insoluble white material also formed.

2. Spectroscopic and Structural Properties. Complex $1^+BF_4^-$ was characterized by microanalysis and IR, NMR (^1H, ^{13}C, ^{31}P), and UV/visible spectroscopy. Data are summarized in the Experimental Section. All preparations gave $1^+BF_4^-$ as a 95:5 mixture of *RS,SR/RR,SS* diastereomers (**II/III**, Scheme 1), as assigned from ^{31}P and ^1H NMR chemical shift trends established for other π aldehyde complexes of **I** (^{31}P (ppm) 10.7/11.1 (CD_2Cl_2), 12.0/12.4 (CD_3CN); ^1H (δ) 6.19/6.02 (CD_2Cl_2 or CD_3CN))[6,8] and additional experiments below.

Consistent with the usual shielding trends in metal π complexes, the ^1H and ^{13}C NMR signals of the coordinated O=CH moiety (*RS,SR*, CD_3CN: δ 5.32, 69.0 ppm) were upfield of those of the free O=CH moiety (δ 9.05, 197.0 ppm). The IR ν_{NO} value (1749 cm^{-1}) closely matched that of acrolein complex $2^+BF_4^-$ (1748 cm^{-1}). The IR $\nu_{C=O}$ value of the uncoordinated carbonyl group (1699 cm^{-1}) was close to that of free acrolein (1704 cm^{-1}) but lower than that of glyoxal (1737–1746 cm^{-1}).[2b] The UV/visible spectrum showed no absorptions with a λ_{max} of ≥300 nm.

Compounds with X=C(R)—(R′)C=X′ linkages are capable of *s-cis/s-trans* isomerism, as illustrated for *(RS,SR)*-$1^+BF_4^-$ in Scheme 3. Glyoxal is predominantly an *s-trans* conformer in the gas phase and argon matrices.[2,14] We have previously studied such equilibria for enone, enal, and diene adducts of **I** in solution.[8,9] The $^3J_{HH}$ values for the O=C***H*** protons of $1^+BF_4^-$, 4.5–5.1 Hz (CD_3CN, CD_2Cl_2), are intermediate between those proposed earlier for *s-cis* and *s-trans* isomers,[8] suggesting appreciable populations of each. Hence, a ^1H difference NOE experiment was conducted.[15] As shown in Scheme 3, when the coordinated O=C***H*** resonance was irradiated, a 6.6% enhancement occurred in the free O=C***H*** resonance. This indicates that a significant amount of the *s-cis* isomer is present. A 5.1% enhancement also occurred in the cyclopentadienyl resonance. This confirms the diastereomer assignment.

We next sought to determine the solid state structure of $1^+BF_4^-$. Crystallization gave yellow prisms of diastereomerically pure *(RS,SR)*-$1^+BF_4^-$, and X-ray data were collected as outlined in Table 1. Refinement included the location of the two O=C***H*** hydrogens and gave the structures shown in Figure 1. Atomic coordinates and selected bond lengths and angles are summarized in Tables 2 and 3.

Figure 1 shows that the glyoxal ligand adopts an *s-cis* conformation in the solid state, with a O1—C1—C2—O2 torsion angle of 4.6(1.7)°. As expected, the coordinated O=C bond (1.331(5) Å) was longer than the free O=C bond (1.206(7) Å). The latter was close to the O=C bond length in free glyoxal (1.202(12) Å), which has been determined from microwave and electron diffraction studies.[16] The sum of the C—C—O, H—C—C, and H—C—O bond angles about the free O=CH carbon was 359°, consistent with an sp^2 trigonal planar geometry.

Table 1. Summary of Crystallographic Data for *(RS,SR)*-$1^+BF_4^-$

mol formula	$C_{25}H_{22}BF_4NO_3PRe$
mol wt	688.44
cryst syst	monoclinic
space group	$P2_1/a$ (No. 14)
cell dimens	
a, Å	14.396(1)
b, Å	17.827(2)
c, Å	9.734(1)
β, deg	98.34(1)
V, Å^3	2471.67
Z	4
d_{calcd}, g/cm^3 (15 °C)	1.850
d_{obs}, g/cm^3 (23 °C)	1.848
cryst dimens, mm	0.33 × 0.30 × 0.15
diffractometer	Syntex $P\bar{1}$
radiation, Å	λ(Mo Kα) 0.710 73
data collcn method	θ–2θ
scan speed, deg/min	3.0
no. of reflns measd	4787
range/indices (h,k,l)	0–17, 0–21, −11 to +11
scan range	$K\alpha_1$ −1.0 to $K\alpha_2$ +1.0
no. of reflns between stds	98
total no. of unique data	4517
no. of obsd data, $I > 3\sigma(I)$	3358
abs coeff (μ), cm^{-1}	51.028
min transm, %	51.70
max transm, %	99.90
no. of variables	331
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0373
$R_w = \sum(\|\|F_o\| - \|F_c\|\|)w^{1/2}/\sum\|F_o\|w^{1/2}$	0.0461
goodness of fit	5.3779
Δ/σ (max)	0.003
$\Delta\rho$ (max), e/Å^3	1.302, 1.37 Å from Re

The sum of the analogous bond angles about the coordinated O=CH carbon was 350°, indicating moderate rehybridization. A plane was defined that contained the coordinated O=C moiety and was perpendicular to the Re–O=C plane. The angle of the C—C bond with the plane ("bend-back" angle) was 27.4°.

The angles of the Re–O=C plane with the Re—P and Re—N bonds were 13.0 and 71.8°, respectively. This indicates a slight deviation from the idealized structure **II** (Scheme 1), in which the corresponding angles are 0 and 90°. The angle of the Re–O=C plane with that defined by the cyclopentadienyl centroid, rhenium, and O=C centroid was 64.9°. As observed with other π aldehyde complexes of **I**, the rhenium was considerably closer to the more electronegative oxygen (2.056(3) Å) than to carbon (2.129(5) Å). A slippage value of 17% was calculated, as defined and discussed elsewhere.[4b,6b]

3. Reactivity. The NMR signals of the *RS,SR/RR,SS* diastereomers of $1^+BF_4^-$ did not coalesce at 100 °C in CD_3CN. This bounds $\Delta G^{\ddagger}$ (100 °C) for any process capable of interconverting the diastereomers as ≥20.0 kcal/mol.[17] However, since all syntheses and workup conditions give a 95:5 ratio of diastereomers, we presume that a dynamic equilibrium exists. This could involve either exchange of the O=C enantioface bound to rhenium or a migration of rhenium along the O=C—C=O moiety.[18]

Aldehyde complexes of **I** undergo diastereoselective additions with cyanide ion and other nucleophiles.[4a,7] However, we were unable to effect similar well-defined reactions with $1^+BF_4^-$. For example, PPN^+CN^- (1.0 equiv)

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(17) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 66. The $\Delta G^{\ddagger}$ calculation utilized eq 6.5c (as opposed to 6.7a) and the uncoordinated O=C***H*** ^1H resonances.

(18) This possibility is diagramed in Scheme VII of ref 9.

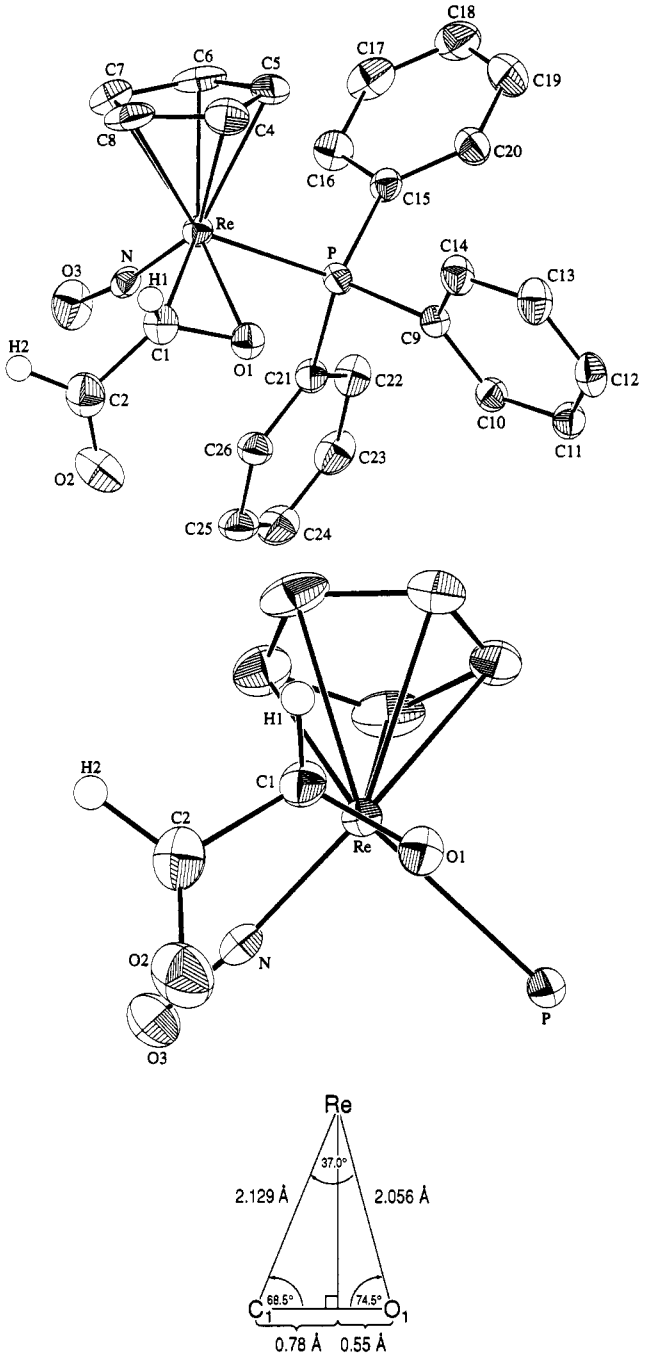


Figure 1. Structure of the cation of (*RS,SR*)-$1^+BF_4^-$: (top) numbering diagram; (middle) Newman-type projection with phenyl rings omitted; (bottom) view of the Re–O–C plane.

and $1^+BF_4^-$ were combined in CH_2Cl_2 in an NMR tube at −80 °C. Subsequent ^{31}P NMR spectra showed the formation of numerous products (major, −80 °C: 18.9 ppm, 48% of integral trace). After several hours at room temperature, the principal product was the cyanide complex (η^5-C_5H_5)Re(NO)(PPh_3)(CN) (17.9 ppm, ca. 30%).[11a] Similarly, we were unable to effect hydride additions under conditions utilized previously.[4a] No reaction occurred when $1^+BF_4^-$ and Me_3SiCN were combined (CH_2Cl_2, 3 days).

We sought to displace the glyoxal ligand from $1^+BF_4^-$. According to procedures developed earlier with the formaldehyde complex $3^+BF_4^-$,[10] $1^+BF_4^-$ and aqueous NaI were combined in acetonitrile (Scheme 4). The iodide salt 1^+I^- precipitated in 75% yield. This compound was insoluble in all common organic solvents investigated except DMSO. When 1^+I^- was placed in methanol, a rapid reaction occurred. Workup gave the previously characterized iodide complex (η^5-C_5H_5)Re(NO)(PPh_3)(I) (**6**)[19] in 69% yield. An identical reaction was conducted in methanol-d_4 in an NMR tube. However, no ^1H resonance

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for (*RS,SR*)-$1^+BF_4^-$ [a]

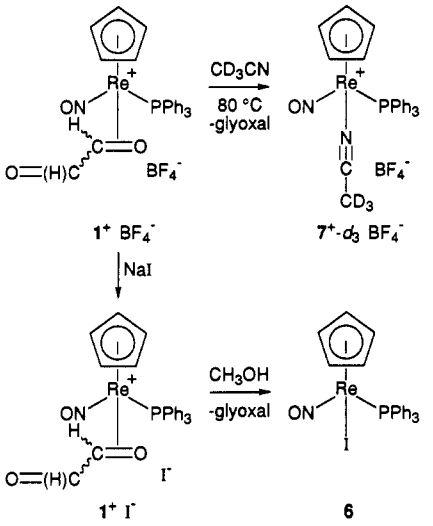
atom	*x*	*y*	*z*	*B* (Å²)
Re	0.03104(3)	0.21353(2)	0.21679(4)	2.833(6)
P	0.0135(2)	0.3309(1)	0.3430(2)	2.89(5)
O1	−0.1058(4)	0.2061(4)	0.2534(6)	3.6(1)
O2	−0.1978(6)	0.2151(6)	−0.0202(9)	6.9(2)
O3	0.0357(6)	0.2953(5)	−0.0431(8)	5.8(2)
N	0.0269(5)	0.2646(4)	0.0626(8)	3.0(2)
C1	−0.0964(7)	0.1533(6)	0.160(1)	3.8(2)
C2	−0.1455(8)	0.1635(7)	0.015(1)	5.2(3)
C4	0.0861(8)	0.1137(6)	0.359(1)	4.6(3)
C5	0.1414(8)	0.1760(7)	0.399(1)	4.9(3)
C6	0.1859(7)	0.1997(7)	0.284(1)	5.4(3)
C7	0.1606(8)	0.1502(7)	0.174(1)	5.0(3)
C8	0.1034(7)	0.0983(6)	0.222(1)	5.4(3)
C9	−0.0636(6)	0.3240(5)	0.4751(9)	3.1(2)
C10	−0.1214(7)	0.3830(6)	0.500(1)	3.4(2)
C11	−0.1729(7)	0.3787(6)	0.607(1)	4.0(2)
C12	−0.1678(8)	0.3165(7)	0.691(1)	4.4(2)
C13	−0.1092(9)	0.2580(7)	0.668(1)	4.8(3)
C14	−0.0585(8)	0.2608(6)	0.561(1)	4.2(2)
C15	0.1242(7)	0.3682(5)	0.430(1)	3.3(2)
C16	0.1915(8)	0.3934(6)	0.352(1)	4.6(2)
C17	0.2756(8)	0.4219(7)	0.419(1)	5.5(3)
C18	0.2940(8)	0.4246(7)	0.561(1)	6.0(3)
C19	0.2289(9)	0.3999(9)	0.636(1)	6.8(4)
C20	0.1444(8)	0.3704(8)	0.573(1)	5.0(3)
C21	−0.0380(7)	0.4064(5)	0.226(1)	3.3(2)
C22	−0.0042(8)	0.4795(6)	0.247(1)	4.1(2)
C23	−0.0473(9)	0.5358(6)	0.161(1)	5.1(3)
C24	−0.1201(9)	0.5186(7)	0.059(1)	5.3(3)
C25	−0.1524(7)	0.4475(7)	0.039(1)	4.5(2)
C26	−0.1101(7)	0.3907(6)	0.123(1)	3.7(2)
B	0.425(1)	0.5795(8)	0.217(1)	4.8(3)
F1	0.4974(8)	0.5857(9)	0.150(1)	14.7(4)
F2	0.4571(9)	0.5427(8)	0.336(1)	12.7(4)
F3	0.3679(9)	0.5344(7)	0.145(1)	15.7(4)
F4	0.388(1)	0.6407(7)	0.240(2)	9.6(5)
H1	1.096(8)	0.895(7)	0.82(1)	5.0
H2	1.127(8)	0.882(7)	1.05(1)	5.0

[a] Atoms refined anisotropically are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) in (*RS,SR*)-$1^+BF_4^-$

Re–P	2.458(1)	P–C15	1.820(4)
Re–N	1.749(4)	P–C21	1.850(4)
N–O3	1.188(4)	O1–C1	1.331(5)
Re–O1	2.056(3)	O2–C2	1.206(7)
Re–C1	2.129(5)	C1–C2	1.494(7)
Re–C4	2.321(5)	C4–C5	1.390(7)
Re–C5	2.305(5)	C4–C8	1.414(8)
Re–C6	2.245(4)	C5–C6	1.431(8)
Re–C7	2.271(5)	C6–C7	1.401(8)
Re–C8	2.301(5)	C7–C8	1.368(7)
P–C9	1.821(4)	C9–C10	1.383(6)
P–Re–N	89.6(1)	Re–P–C21	111.8(1)
Re–N–O3	171.2(3)	O1–C1–C2	118.6(5)
P–Re–O1	78.33(9)	O2–C2–C1	123.4(5)
P–Re–C1	114.4(1)	H1–C1–O1	122(4)
N–Re–C1	96.8(2)	H1–C1–C2	109(4)
N–Re–O1	105.5(1)	H2–C2–O2	127(3)
O1–Re–C1	37.0(1)	H2–C2–C1	109(3)
Re–O1–C1	74.5(2)	C4–C5–C6	108.4(5)
Re–C1–O1	68.5(2)	C4–C8–C7	113.0(5)
Re–C1–C2	117.1(3)	C5–C4–C8	104.6(5)
Re–P–C9	114.4(1)	C5–C6–C7	108.7(5)
Re–P–C15	113.4(1)	C6–C7–C8	105.2(5)

Scheme 4. Reactions of Glyoxal Complex $1^+BF_4^-$



for free glyoxal was detected (δ 4.32, 4.30, 2s). Presumably, some type of methanol addition product forms, several of which are known.[20]

Next, $1^+BF_4^-$ and $(n\text{-Bu})_4N^+I^-$ were combined in an NMR tube in $CDCl_3$. The former was sparingly soluble, and only a very slow reaction occurred. After several days, ca. 29% conversion to iodide complex **6** had occurred, as assayed by integration of the cyclopentadienyl ^1H resonance vs. $(n\text{-Bu})_4N^+$ ^1H resonances. Traces of monomeric glyoxal were present (δ 9.33). Constant shaking or sonication did not give faster substitution rates.

The formaldehyde ligand in $3^+BF_4^-$ is also slowly displaced by acetonitrile at room temperature.[10] Thus, $1^+BF_4^-$ and CD_3CN were combined in an NMR tube, and ^1H spectra were recorded. No reaction occurred at room temperature, so the sample was warmed. After 51 h at 80 °C, a 41:59 mixture of $1^+BF_4^-$ and the deuterioacetonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCD_3)]^+BF_4^-$ ($7^+\text{-}d_3$ BF_4^-)[11] remained in solution. Some black material precipitated concurrently. After 108 h, a 10:90 $1^+BF_4^-$/$7^+\text{-}d_3$ BF_4^- mixture was present. After 170 h, workup gave $7^+\text{-}d_3$ BF_4^- in 50% yield. At no time was any free glyoxal detected, although a new singlet appeared at δ 4.06.

Discussion

As summarized in Scheme 3, two viable routes to glyoxal complex $1^+BF_4^-$ have been developed. The first is an empirically optimized recipe that utilizes methanolic aqueous glyoxal. Since this solution contains a complex equilibrium mixture of ethereal and hydroxylic oxygen donor ligands,[1,20] it is surprising that $1^+BF_4^-$ is obtained at all. Water and alcohol complexes of the rhenium fragment **I** have been isolated previously.[21] Importantly, aldehydes react with the latter to give aldehyde complexes.

The second route is analogous to those used for other aldehyde complexes of **I**. However, we were surprised by the ease with which anhydrous monomeric glyoxal can be generated from the trimeric dihydrate and P_2O_5. All literature on glyoxal can be easily retrieved via on-line data bases, and we have been unable to locate previous preparative applications of this pyrolytic synthesis. Furthermore, it is easily conducted on a large scale.

Theoretical studies of alkali and alkaline earth metal complexes of glyoxal have been reported.[22] However, to our knowledge $1^+BF_4^-$ is the first metal complex of any dialdehyde to be isolated. Nonchelating adducts allow internal comparisons of the physical and chemical properties of free and coordinated O=CH moieties. We sought to prepare the corresponding malonaldehyde complex, in which the two O=CH groups would not be directly linked. However, using published recipes for the free ligand,[23] we obtained crude products that appeared to be enolic. These could not in our hands be purified. Some conceptually related compounds that have been isolated include the ethane-1,2-dionyl or μ-oxalyl complex $(CO)_5Re\text{—}C(=O)\text{—}C(=O)\text{—}Re(CO)_5$,[24] and the μ-malonyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)C(=O)\text{—}CH_2\text{—}C(=O)\text{—}Re(CO)_4$.[25]

Many transition metal complexes serve as "shelf stable" sources of reactive organic molecules. However, we have not yet devised conditions by which glyoxal can be displaced from 1^+X^- under mild conditions in aprotic media. Since other aldehyde ligands are (1) easily displaced from **I** and (2) undergo much more rapid exchange of the enantioface bound to **I**,[6] we believe that the rhenium–glyoxal ligand bond is likely stronger. Indeed, simple Hückel theory predicts that glyoxal should be both a stronger π donor and stronger π acceptor than other aldehydes. We were also unable to effect any well-defined deprotonation of $1^+BF_4^-$, which could have given a ReO—CH=C=O species, or decarbonylation with $Rh(Cl)(PPh_3)_3$ to formaldehyde complex $3^+BF_4^-$.

Aliphatic aldehyde complexes of **I** give higher equilibrium ratios of *RS,SR/RR,SS* diastereomers (≥99:1 **II/III**, Scheme 1)[6] than glyoxal complex 1^+X^- (95:5). For many alkene complexes of **I**, ligands with sp^3-hybridized substituents give higher binding selectivities than analogs with sp^2-hybridized substituents.[9,26] Steric rationales have been proposed. However, acrolein, which is roughly "isosteric" with glyoxal, also gives a higher **II/III** ratio (≥99:1).[8] An exhaustive compilation of data and analysis of trends will appear in the near future.[6b]

In summary, we have demonstrated that a pyrolytic procedure previously employed to generate anhydrous monomeric glyoxal in the gas phase or argon matrices can be adapted for preparative chemistry. We have also prepared the first transition metal complex of glyoxal and defined its basic physical and chemical properties.

Experimental Section

General Data. General procedures were identical with those given in a recent paper.[5] NMR spectra were referenced as follows: ^1H (δ), TMS (0.00), CD_2HCN (1.93), or CD_2HSOCD_3 (2.49); $^{13}C\{^1H\}$ (ppm), CD_3CN (1.3); $^{31}P\{^1H\}$ (ppm), external 85% H_3PO_4 (0.0). All coupling constants (*J*) are in hertz. The ^1H NOE difference spectrum was acquired as described earlier (94%

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saturation, septum sealed tube).[27] Chlorinated solvents and CD_3CN were distilled from P_2O_5 or CaH_2, and ether was distilled from Na/benzophenone. $HBF_4{\cdot}OEt_2$ (Aldrich) was standardized with *N,N*-dimethylaniline.[28] Other solvents and reagents were used as received from common commercial sources.

Anhydrous Monomeric Glyoxal. A round-bottom flask was charged with trimeric glyoxal dihydrate (0.54 g, 2.6 mmol) and P_2O_5 (1.4 g) and heated to 160 °C under oil-pump vacuum. The volatiles were collected in a Schlenk flask that had been cooled to −80 °C. Then $CDCl_3$, CH_2Cl_2, or THF was added to dissolve the resulting light yellow-green solid. Titers were established as described in the text. NMR ($CDCl_3$): ^1H (δ) 9.30; $^{13}C\{^1H\}$ (ppm) 188.2 ppm. UV/visible (nm (ϵ, $M^{-1}\,cm^{-1}$), ca. 0.013 M in THF): 278 (ca. 64), 426 (ca. 9.5).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHCH{=}O)]^+BF_4^-$ ($1^+BF_4^-$). A. A Schlenk tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (4;[29] 336 mg, 0.602 mmol), CH_2Cl_2 (1 mL), and a stir bar, and the mixture was cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (70 μL, 0.65 mmol) was added with stirring to generate $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ ($5^+BF_4^-$).[11a] After 5 min, a solution of aqueous glyoxal (40%; 350 μL, 3.07 mmol) in methanol (1 mL) was added. The mixture was allowed to slowly warm to room temperature (ca. 4 h) and was then added to ether (150 mL). After 3 h, hexane (100 mL) was added. After 1 h, the supernatant was removed from the resulting light pink solid by pipet. The solid was washed with THF (2 × 10 mL) and CH_2Cl_2 (2 × 10 mL) and then dissolved in acetone (30 mL). The solution was filtered through a pipet containing a glass fiber plug. The filtrate was concentrated to ca. 10 mL and filtered through a glass fiber plug again. The filtrate was added to ether (80 mL). The resulting tan powder was collected by filtration, washed with ether, and dried under oil-pump vacuum to give $1^+BF_4^-$ (69 mg, 0.100 mmol, 17%; 95:5 *RS,SR/RR,SS*). B. A similar reaction was conducted with **4** (115 mg, 0.206 mmol), CH_2Cl_2 (1.5 mL), $HBF_4{\cdot}OEt_2$ (24 μL, 0.22 mmol), and a freshly prepared anhydrous glyoxal (1.6 mmol in 1.5 mL of CH_2Cl_2; assayed by ^1H NMR in $CDCl_3$). An identical workup gave $1^+BF_4^-$ (43 mg, 0.062 mmol, 33%; 95:5 *RS,SR/RR,SS*), mp 227–234 °C dec. IR (cm^{-1}, KBr/thin film): ν_{NO} 1757/1749 (vs), $\nu_{C=O}$ 1697/1699 (s). UV/visible (nm (ϵ, $M^{-1}\,cm^{-1}$), 6.25×10^{-5} M in CH_3CN): 268 (sh, 1.07×10^4), 276 (sh, 9.12×10^3). Anal. Calcd for $C_{25}H_{22}BF_4NO_3PRe$: C, 43.62; H, 3.22. Found: C, 43.70; H, 3.30.

NMR, *RS,SR*: ^1H (δ, CD_3CN/CD_2Cl_2) 9.05/8.94 (d, J_{HH} = 4.5/5.1, free O=CH), 7.72–7.46 (m, $3C_6H_5$), 6.19/6.19 (d/s, J_{HP} = 0.6, C_5H_5), 5.32/5.33 (dd, J_{HH} = 4.5/5.1, J_{HP} = 1.8/1.8, bound O=CH); $^{13}C\{^1H\}$ (ppm, CD_3CN) 197.0 (s, free O=CH), 134.7 (d, J_{CP} = 10.6, *o*-Ph), 134.2 (d, J_{CP} = 2.7, *p*-Ph), 130.8 (d, J_{CP} = 12.3, *m*-Ph), 127.3 (d, J_{CP} = 61.4, *i*-Ph), 101.8 (s, C_5H_5), 69.0 (d, J_{CP} = 1.1, bound O=CH); $^{31}P\{^1H\}$ (ppm, CD_3CN/CD_2Cl_2) 12.0/10.7 (s). NMR, *RR,SS*: ^1H (δ, CD_3CN/CD_2Cl_2) 9.28/9.49 (d, J_{HH} = 4.5/4.2, free O=CH), 7.72–7.46 (m, $3C_6H_5$), 6.02/6.02 (d/s, J_{HP} = 0.9, C_5H_5), 5.05/5.04 (dd, J_{HH} = 4.5/4.2, J_{HP} = 1.2/0.9, bound O=CH); $^{13}C\{^1H\}$ (ppm, CD_3CN, partial) 101.7 (s, C_5H_5); $^{31}P\{^1H\}$ (ppm, CD_3CN/CD_2Cl_2) 12.4/11.1 (s).

1^+I^-. A flask was charged with $1^+BF_4^-$ (39 mg, 0.057 mmol) and CH_3CN (2 mL). Then NaI (2.0 M aqueous solution; 85 μL, 0.17 mmol) was added. The mixture was kept at room temperature without stirring. After 12 h, the supernatant was removed from the resulting yellow crystals by pipet. The crystals were washed with acetone (2 × 1 mL) and ether (2 × 1 mL) and dried under oil-pump vacuum to give 1^+I^- (31 mg, 0.043 mmol, 75%; 95:5 *RS,SR/RR,SS*), mp 246–255 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1757 (vs), $\nu_{C=O}$ 1696 (m). Anal. Calcd for $C_{25}H_{22}INO_3PRe$: C, 41.22; H, 3.05; I, 17.42. Found: C, 41.17; H, 3.05; I, 17.48.

NMR, *RS,SR/RR,SS* (DMSO): ^1H (δ) 9.06/9.19 (d, J_{HH} = 4.2/4.2, free O=CH), 7.73–7.45 (m, $3C_6H_5$), 6.52/6.32 (s, C_5H_5), 5.53/5.21 (dd, J_{HH} = 4.2/4.2, J_{HP} = 1.8/1.2, bound O=CH); $^{31}P\{^1H\}$ (ppm) 12.5/12.7 (s).

Reactions of 1^+X^-. The following are representative. A. A flask was charged with 1^+I^- (19 mg, 0.026 mmol) and a stir bar. Then methanol (1 mL) was added with stirring. The yellow solid gradually dissolved as a purple precipitate formed. After 2 h, the supernatant was removed by pipet. The purple solid was washed with ether (2 × 1 mL) and dried under oil-pump vacuum to give $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (12 mg, 0.018 mmol, 69%). The IR and $^1H/^{31}P$ NMR spectra were identical with those of an authentic sample.[19] B. A 5-mm NMR tube was charged with $1^+BF_4^-$ (43 mg, 0.062 mmol) and CD_3CN (0.6 mL) and capped with a septum. The solution was kept at 80 °C and periodically monitored by ^1H NMR (data: see text). After 170 h, the sample was decanted into ether (20 mL), leaving a black residue in the tube. A yellow precipitate formed, and the supernatant was removed by pipet. The solid was washed with ether (2 × 2 mL) and dried under oil-pump vacuum to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCD_3)]^+BF_4^-$ ($7^+\text{-}d_3\ BF_4^-$; 21 mg, 0.031 mmol, 50%). The $^1H/^{31}P$ NMR spectra were identical with those of an authentic sample.[11a]

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CH_2)]^+BF_4^-$ ($3^+BF_4^-$). A Schlenk flask was charged with **4** (156 mg, 0.279 mmol), some solid $MgSO_4$, CH_2Cl_2 (4 mL), and a stir bar, and the mixture was cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (32 μL, 0.30 mmol) was added with stirring. After 5 min, aqueous formaldehyde (37%, 65 μL, 0.88 mmol) was added, and the cold bath was removed. After 3 h, the mixture was filtered through a pipet containing a glass fiber plug. The filtrate was added to ether (100 mL). The resulting tan powder was collected by filtration, washed with ether, and dried under oil-pump vacuum to give $3^+BF_4^-$ (99 mg, 0.150 mmol, 54%). The IR and $^1H/^{31}P$ NMR spectra were identical with those of an authentic sample.[10]

Crystallography. A yellow prism of *(RS,SR)*-$1^+BF_4^-$ was grown by slow vapor diffusion of ether into an acetonitrile solution, and data were collected as outlined in Table 1. Cell constants were obtained from 50 reflections with $10° < 2\theta < 20°$. The space group was determined from systematic absences (*h0l*, *h* = 2n; *0k0*, *k* = 2n) and subsequent least-squares refinement. Lorentz, polarization, and empirical absorption (ψ scans) corrections were applied. The structure was solved by the standard heavy-atom techniques with SPD/VAX package.[30] Non-hydrogen atoms were refined with anisotropic thermal parameters. The BF_4^- anion exhibited some high thermal motion and disorder. Hydrogen atoms on C1 and C2 were located and refined. Other hydrogen atom positions were calculated and added to the structure factor calculations but not refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[31]

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Supplementary Material Available: Table of anisotropic thermal parameters for *(RS,SR)*-$1^+BF_4^-$ (1 page). Ordering information is given on any current masthead page.

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