−197.1 ppm for F(1) lends some support to this notion. Alternatively, this C–F bond lengthening and high-field ^{19}F chemical shift may be due to a rehybridization by C(1) such that more p character is found in the orbital used to form the bond to F(1), or they may reflect a significant ionic contribution in the Co–C bonding.[1] There is a pronounced flattening of the tetrahedron involving Co, C(1), C(2), and C(2a) (Co–C(1)–C(2) = 116.0 (2)°; summation of the angles involving these atoms is 343.3°; F(1)–C(1)–C(2) = 101.7 (3)°) suggesting that more s character might be utilized in the C–C bonds. However, the C(1)–C(2) bond distance is 1.532 (5) Å, which would seem to argue against rehybridization. Thus, the best explanation at this time would appear to be that there is significant carbanionic character involving the carbon atom bonded to the cobalt atom.

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Supplementary Material Available: Tables of crystallographic, intensity, and structure solution and refinement data, bond lengths and angles, thermal parameters, and hydrogen atom coordinates (3 pages); a listing of structure factors for $pyCo(DH)_2[CF(CF_3)_2]$ (7 pages). Ordering information is given on any current masthead page.

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Reduction Pathways in Lateral and Diagonal $(\eta^5\text{-}C_5Me_5)Re(CO)_2Br_2$. Synthesis, Structure, and Reactivity of $[(\eta^5\text{-}C_5Me_5)Re(CO)_2Br^-]$

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The rhenium anion $[(\eta^5\text{-}C_5Me_5)Re(CO)_2Br^-]$ (**2**$^-$) has been prepared in high yield from the reaction of lateral or diagonal $(\eta^5\text{-}C_5Me_5)Re(CO)_2Br_2$ (**1**) with alkyl/aryllithium and Grignard reagents, trialkylborohydrides, and one-electron reducing agents. The molecular structure of **2**$^-$ (as the [PPP$^+$] salt) was established by X-ray crystallography. $[(\eta^5\text{-}C_5Me_5)Re(CO)_2Br][PPP]$ crystallizes in the orthorhombic space group *Pbca* with $a = 20.646$ (5) Å, $b = 17.690$ (5) Å, $c = 17.555$ (3) Å, $V = 6412$ Å^3, and $Z = 8$. Solution FT-IR studies of **2**$^-$ (in THF) reveal the presence of only solvent-separated ion pairs when the gegencation is [Li$^+$], [K$^+$], or [PPP$^+$] from −70 °C to room temperature. [**2**][Na] at room temperature displays a 39:61 mixture of carbonyl oxygen–sodium and solvent-separated ion pairs, respectively. Variable-temperature FT-IR examination of [**2**][Na] reveals a reversible temperature-dependent equilibrium involving both anionic species. The equilibrium constant for these ion pairs has been determined by IR band-shape analysis over the temperature range −70 °C to room temperature, and values of ΔH and ΔS are reported. The reactivity and stability of **2**$^-$ are described.

Introduction

Synthetic routes to the (cyclopentadienyl)dicarbonylrhenium dihalide compounds $CpRe(CO)_2X_2$ (where X = Br, I) have been known for several years.[1-4] Of these dihalides, the dibromide has received much attention in terms of chemical investigation[5] and as a precursor in the synthesis of other four-legged piano-stool complexes based on the CpRe fragment.[6-13] However, synthetic pathways to the corresponding (pentamethylcyclopentadienyl)dicarbonylrhenium dihalides, $Cp^*Re(CO)_2X_2$ (where Cp* = C_5Me_5), have only recently been described in detail. While the diiodide $Cp^*Re(CO)_2I_2$, initially obtained from the reaction of $Cp^*_2Re_2(CO)_5$ with I_2, was the first compound of this genre prepared,[14] it was not until the work of Sutton et al. that reliable and stereoselective syntheses of these dihalide compounds were reported.[15-18] As such, the reactivity of these dihalides remains to be explored and established. Four-legged piano-stool complexes of the form $CpMX_2Y_2$ may exist as two nonequivalent stereoisomers that are commonly referred to as *cis* and *trans* isomers. We have adopted King's nomenclature[2] to describe the isomeric dibromides discussed in this paper. Here the descriptors lateral and diagonal correspond to the cis and trans stereoisomers, respectively.

The reaction of $CpRe(CO)_2Br_2$ with Grignard reagents has been reported.[6] However, no mention was made of the relationship between the product dependence and initial dibromide stereochemistry. Furthermore, while the reported physical data dealing with such compounds as $CpRe(CO)_2Br(Me)$, $CpRe(CO)_2I(Me)$, and $CpRe(CO)_2(Me)_2$ are not in question, we do not believe that these represent products of direct alkyl/bromide exchange.

In related reactivity studies using the isomeric dibromides, $CpRe(CO)_2Br_2$, we have observed that a direct metathetical re-

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placement of the bromide ligands with RLi or RMgX reagents (where R = Me, Ph, or *t*-Bu) to yield the dialkyl (aryl) complexes $CpRe(CO)_2R_2$ does not occur.[19,20] Instead, metal–halogen exchange and cyclopentadienyl ring attack are observed. The relative amounts of these products are dependent on the nature of the reducing agent and the stereochemistry of the initial dibromide. For example, *diag*-$CpRe(CO)_2Br_2$ reacts exclusively with RLi and RMgX reagents to afford $[CpRe(CO)_2Br^-]$, while the lateral isomer gives both $[CpRe(CO)_2Br^-]$ and $[(\eta^4\text{-}C_5H_5R)Re(CO)_2Br_2^-]$ with MeLi and PhLi. Therefore, it was of interest to us to examine the chemistry associated with the Cp*Re analogue using similar reducing agents. Here we report our results on the reaction of $Cp^*Re(CO)_3$ with Br_2 as a route toward the isomeric dibromide compounds, the reactivity of *lat*-**1** and *diag*-**1** with a variety of reducing agents, and the thermodynamics of ion pairing in $[Cp^*Re(CO)_2Br][Na]$.

Results

The transformations observed in this work are summarized in eqs 1 and 2 and Scheme I. A structure study was undertaken for [**2**][PPP], whose results are presented in Tables I–III and Figure 2. Finally, ion pairing and functionalization studies of **2**⁻ were conducted and the results are shown in Table IV and Figures 4 and 5. These results are discussed in the appropriate sections that follow.

Discussion

I. Synthesis of *lat*- and *diag*-$Cp^*Re(CO)_2Br_2$. Reaction of either Br_2[1,2] or pyridinium hydrobromide perbromide[9] with $Cp^*Re(CO)_3$[21] in trifluoroacetic acid (TFA) gives the expected isomeric dibromides in low to moderate yields. The length of the reaction appears to be important, as we have repeatedly obtained only *lat*-**1** in 30–40% yield (isolated) during short mixing periods (<1 h). Longer reaction times (1–3 days) give both *lat*-**1** and *diag*-**1** in lowered yields, which are easily isolated in pure form by column chromatography using silica gel.[16] Independent of the reaction's duration is the formation of a green material that is devoid of carbonyl ligands and that has resisted purification via chromatography as it is irreversibly adsorbed onto the silica gel. Tentatively, we believe this material may be the tetrabromide complex Cp^*ReBr_4,[22] which results from bromination of *lat*-**1** and *diag*-**1**. Independent treatment of **1** with pyridinium hydrobromide perbromide leads to formation of a green material that displays a single, new Cp* resonance at δ 1.90 ($CDCl_3$) suggestive of Cp^*ReBr_4.

II. Reaction of 1 with RLi, RMgX, and Trialkylborohydrides. The reduction behavior of *lat*-**1** and *diag*-**1** was initially studied with RLi reagents (R = Me, Ph, *t*-Bu) in an attempt to prepare the corresponding R-substituted complex $Cp^*Re(CO)_2Br(R)$.[23] However, in all cases only the anionic complex $[Cp^*Re(CO)_2Br^-]$ (**2**⁻) was observed when 1 equiv of RLi was used (eq 1). Red-brown solutions of **1** (either isomer) react instantaneously with added RLi at −78 °C in THF to give a yellow solution containing **2**⁻; the essentially quantitative conversion to **2**⁻ was easily confirmed by low-temperature FT-IR measurements. The carbonyl bands for **2**⁻ are observed at 1863 and 1789 cm⁻¹ consistent with the ascription of **2**⁻ as an anionic three-legged piano-stool complex (see Figure 1a). Such a low-energy shifting of the CO stretching bands of **2**⁻ relative to **1** is directly attributed to the increased charge density at the rhenium center, which manifests itself by reducing the CO stretching force constant for each of the CO ligands.[24] The higher frequency CO band (1863 cm⁻¹) in **2**⁻ is readily assigned to a symmetric CO stretching mode, while the lower frequency band (1789 cm⁻¹) corresponds to the antisymmetric CO mode on the basis of group theoretical considerations.[25] IR studies (in THF) indicate that **2**⁻ exists as symmetrically solvated ion pairs possessing idealized C_s symmetry.[26] This is supported by the spectral invariance of **2**⁻ over a wide range of temperatures (−78 °C to room temperature), which serves to rule

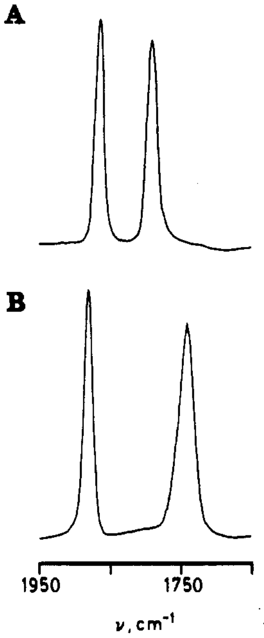
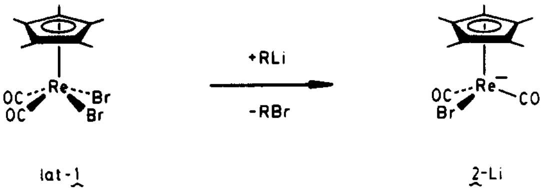


Figure 1. Infrared spectra of the carbonyl region for (A) $[(\eta^5\text{-}C_5Me_5)Re(CO)_2Br][Li]$ and (B) $[(\eta^5\text{-}C_5Me_5)Re(CO)_2Br][MgBr]$. Both spectra were recorded in THF at −70 °C.



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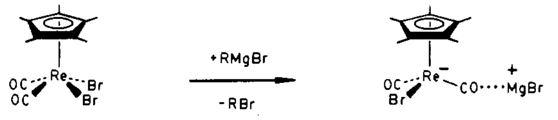
out a dynamic equilibration between different ion pairs.[27] Furthermore, added [Li$^+$] (as CF_3SO_3Li), tetraphenylphosphonium chloride, [PPP][Cl], or 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) do not affect the intensity or frequency of the initial IR spectrum of **2**$^-$, reinforcing the existence of only solvent-separated ion pairs in THF solution.

Complex **2**$^-$ may be easily isolated in high yield by treating [**2**][Li] with [PPP][Cl]. The resulting orange-yellow crystals of [**2**][PPP] gave a satisfactory microanalysis and were used in the NMR characterization of **2**$^-$. The ^{1}H NMR spectrum of [**2**][PPP] in CD_2Cl_2 displayed a singlet at δ 1.94 (15 H) and a multiplet centered at δ 7.75 (20 H) consistent with the methyl groups of the Cp* ring and the aromatic protons of the [PPP$^+$] gegenion, respectively. The $^{13}C\{^1H\}$ NMR spectrum exhibited resonances at δ 11.0, 93.8, and 213.1 for the methyl, Cp* ring, and the carbonyl carbons of **2**$^-$. The metal carbonyl resonance is shifted to lower field relative to either *lat*-**1** and *diag*-**1** as a result of increased charge density at the rhenium center.[28]

Reaction of the Grignard reagents MeMgBr or *t*-BuMgCl with the isomeric dibromides **1** gives **2**$^-$ as a result of metal-halogen exchange. Use of MeMgBr (slight excess) affords **2**$^-$ sluggishly at -78 °C, as determined by low-temperature FT-IR analysis (<10% conversion after 30 min). Warming the solution to room temperature led to the rapid generation of **2**$^-$ (eq 2), which has been characterized in situ by IR spectroscopy (see Figure 1b). [**2**][MgBr] exhibits CO bands at 1872 and 1734 cm^{-1}. These frequencies are different from those observed with [**2**][Li] (vide supra). In comparison to that of [**2**][Li], the symmetric CO stretching band of [**2**][MgBr] is shifted 9 cm^{-1} to higher frequency, while the antisymmetric CO stretching band is shifted 55 cm^{-1} to lower frequency. This behavior is typical of a carbonyl oxygen-[MgBr$^+$] contact ion pair where π-electron density is polarized toward the carbonyl oxygen involved in ion pairing with the [MgBr$^+$] gegencation as shown in eq 2.[26] This interaction is expected to lower the CO stretching frequency of the CO group involved in ion pairing with concomitant strengthening of the remaining CO group.[29]



(2)

The reaction between *t*-BuMgCl and **1** (equimolar amounts) is rapid at -78 °C and gives **2**$^-$ in near quantitative yield.[30] The IR spectrum of [**2**][MgCl] is identical with that of [**2**][MgBr] and suggests similar carbonyl oxygen-[MgX$^+$] contact ion pairs. In reactions with *t*-BuMgCl the possibility exists for a bromide/chloride exchange in the magnesium gegenion. The resulting [MgBr$^+$] cation would be expected to yield an IR spectrum of **2**$^-$ identical with that observed for MeMgBr.

Unequivocal proof for carbonyl oxygen-[MgX$^+$] ion pairs was obtained by examining the effect HMPA had on the solution IR spectrum of [**2**][MgX]. Use of 10 mol equiv of HMPA led to the complete disruption of the contact ion pairs and production of a two-band IR spectrum identical with that of [**2**][Li].

Scheme I

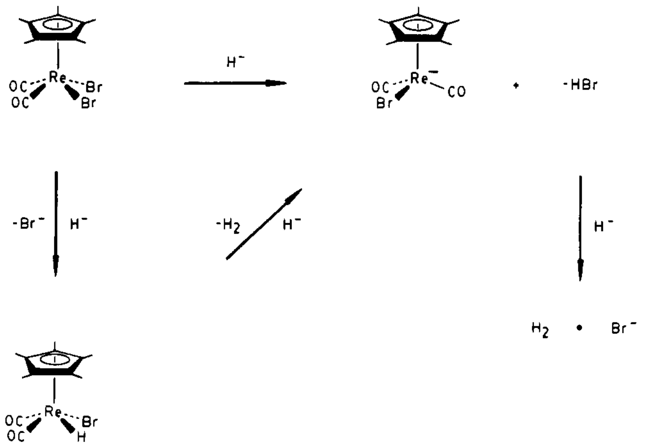


Table I. X-ray Crystallographic and Data Processing Parameters for $[Cp^*Re(CO)_2Br][Ph_4P]$

space group	Pbca/orthorhombic (No. 61)
cell consts	
a, Å	20.646 (5)
b, Å	17.690 (5)
c, Å	17.555 (3)
V, Å^3	6411.6
mol formula	$C_{36}H_{35}BrO_2PRe$
fw	796.76
formula units/cell (*Z*)	8
ρ, g cm^{-1}	1.651
cryst size, mm	0.3 × 0.2 × 0.1
abs coeff (μ), cm^{-1}	51.55
λ(radiatn), Å	0.71073
data collcn method	θ-2θ
collcn range, deg	$2.0° \le 2\theta \le 50.0°$
tot. no. of data collcd	6233
no. of indep data, $I > 3\sigma(I)$	2995
tot. no. of variables	370
R	0.0366
R_w	0.0432
weights	$w = 4F_o^2/[\sigma^2(\text{counting}) + (0.04F_o^2)^2]$

Treatment of **1** with 1.0 mol equiv of Super-H ($LiEt_3BH$) or K-Selectride [K(*sec*-Bu)$_3$BH] at -78 °C led to the immediate formation of **2**$^-$ in 50% yield, as determined by IR analysis (-78 °C). When the hydride concentration was doubled, quantitative conversion to **2**$^-$ was observed. At no time was the presence of the corresponding bromohydride complex Cp*Re(CO)$_2$Br(H) observed (vide infra). On the basis of these observations, we believe, in analogy to the RLi and RMgX reactions, that the hydride reagents react with **1** to give equal molar amounts of **2**$^-$ and HBr. A subsequent, rapid reaction between the generated HBr and excess [R$_3$BH$^-$] would then account for the 1:2 rhenium/hydride stoichiometry observed with this reaction. The hydrogen byproduct necessary for the proposed reaction was observed by GC analysis; however, no attempt was made to quantify it.

An alternative pathway for the rhenium/hydride stoichiometry involves the metathetical replacement of a bromide ligand in **1** to give Cp*Re(CO)$_2$Br(H). Since most metal hydrides are known to exhibit acidic character,[31] a fast follow-up reaction involving metal-hydride deprotonation by additional [H$^-$] would also give **2**$^-$, as outlined in Scheme I. The IR spectra of **2**$^-$ from these reactions are unexceptional when compared with those obtained

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Table II. Positional Parameters for Non-Hydrogen Atoms for $[Cp^*Re(CO)_2Br][Ph_4P]$ with Estimated Standard Deviations in Parentheses[a]

atom	*x*	*y*	*z*	*B*, Å^2
Re	0.64733 (2)	0.10035 (3)	0.61146 (3)	2.904 (7)
Br	0.74495 (6)	0.03683 (7)	0.68025 (8)	4.26 (3)
P	0.0909 (1)	0.6040 (2)	0.0984 (2)	2.65 (5)
O(1)	0.5710 (5)	0.1711 (6)	0.7393 (5)	5.7 (2)
O(2)	0.7146 (5)	0.2484 (6)	0.5771 (6)	6.6 (2)
C(1)	0.6035 (7)	0.1453 (7)	0.6965 (7)	4.1 (3)
C(2)	0.6927 (6)	0.1953 (7)	0.5915 (7)	4.3 (3)
C(3)	0.5981 (6)	0.1021 (8)	0.4961 (7)	4.3 (3)
C(3′)	0.595 (1)	0.1694 (9)	0.4441 (9)	7.9 (4)
C(4)	0.5531 (6)	0.0824 (8)	0.5528 (9)	6.1 (3)
C(4′)	0.4887 (8)	0.122 (1)	0.573 (1)	13.3 (6)
C(5)	0.5714 (6)	0.0079 (8)	0.5848 (7)	5.1 (3)
C(5′)	0.5359 (8)	−0.042 (1)	0.644 (1)	10.7 (5)
C(6)	0.6272 (6)	−0.0155 (7)	0.5457 (7)	3.6 (3)
C(6′)	0.6648 (9)	−0.0888 (8)	0.556 (1)	7.8 (5)
C(7)	0.6446 (6)	0.0419 (7)	0.4926 (6)	3.8 (2)
C(7′)	0.6994 (7)	0.036 (1)	0.4315 (8)	6.7 (4)
C(11)	0.1250 (5)	0.5125 (6)	0.0820 (6)	2.9 (2)
C(12)	0.1398 (6)	0.4654 (7)	0.1452 (7)	3.6 (2)
C(13)	0.1675 (6)	0.3928 (7)	0.1327 (7)	4.3 (3)
C(14)	0.6770 (6)	0.1330 (8)	0.9447 (8)	4.5 (3)
C(15)	0.1603 (5)	0.4163 (7)	−0.0055 (7)	4.2 (3)
C(16)	0.1345 (6)	0.4878 (6)	0.0063 (7)	3.4 (2)
C(21)	0.0149 (5)	0.5929 (6)	0.1479 (6)	2.7 (2)
C(22)	−0.0130 (6)	0.5206 (7)	0.1498 (7)	3.6 (3)
C(23)	−0.0746 (6)	0.5143 (7)	0.1857 (7)	3.6 (3)
C(24)	−0.1031 (6)	0.5762 (8)	0.2174 (7)	4.3 (3)
C(25)	0.5741 (7)	0.3509 (7)	0.7158 (8)	4.5 (3)
C(26)	−0.0143 (6)	0.6564 (7)	0.1794 (7)	4.0 (3)
C(31)	0.1449 (5)	0.6645 (6)	0.1513 (6)	2.7 (2)
C(32)	0.1395 (6)	0.7436 (7)	0.1390 (8)	4.4 (3)
C(33)	0.1802 (7)	0.7925 (8)	0.1816 (8)	5.0 (3)
C(34)	0.2234 (6)	0.7632 (8)	0.2342 (7)	4.1 (3)
C(35)	0.2270 (6)	0.6852 (8)	0.2470 (7)	4.4 (3)
C(36)	0.1879 (6)	0.6356 (7)	0.2048 (7)	3.4 (3)
C(41)	0.0761 (5)	0.6467 (6)	0.0069 (6)	2.8 (2)
C(42)	0.0147 (6)	0.6492 (7)	−0.0223 (7)	3.6 (3)
C(43)	0.0061 (6)	0.6761 (7)	−0.0973 (7)	4.1 (3)
C(44)	0.0596 (7)	0.7033 (8)	−0.1373 (7)	4.9 (3)
C(45)	0.6194 (7)	−0.2025 (9)	1.1060 (8)	5.5 (3)
C(46)	0.6312 (6)	−0.1725 (8)	1.0316 (7)	4.6 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

from the RLi reactions. This suggests that the presence of R_3B, an effective Lewis acid, in solution does not perturb the local environment of the rhenium anion.

III. X-ray Crystallography Structure of [2][PPP]. The structure of $[2^-]$[PPP] has been confirmed by single-crystal X-ray diffraction analysis. Yellow crystals of 2^- were grown from a THF solution containing [PPP][Cl] that had been layered with heptane. [2][PPP] exists as discrete molecules in the unit cell with no unusually short inter- or intramolecular contacts; the $[PPP^+]$ gegenion is unexceptional and requires no further description.[32] The X-ray data collection and processing parameters for 2^- are given in Table I with the final fractional coordinates listed in Table II.

The ORTEP diagram in Figure 2 shows the molecular structure of 2^- and clearly establishes the six-coordinate geometry about the rhenium, assuming the Cp* ring functions as a three-coordinate ligand, and an overall geometry that is typical of three-legged piano-stool complexes.[33] Selected bond distances and angles are given in Table III. The top view of 2^- reveals an approximate mirror plane of symmetry that is defined by the plane formed by the Re–Br and C(6)–C(6′) bonds. This plane bisects the two carbonyl groups and the C(3)–C(4) bond of the Cp* ring. The Re–Br, Re–carbonyl, and C–O bond lengths are unexceptional in comparison to those of other cyclopentadienylrhenium com-

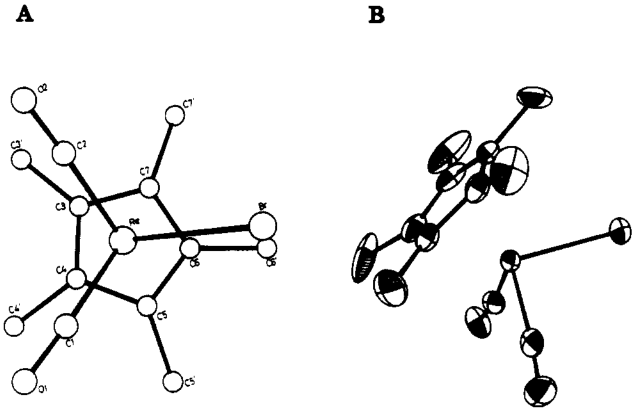

Figure 2. Two ORTEP representations of $[(\eta^5\text{-}C_5Me_5)Re(CO)_2Br][PPP]$: (A) top view; (B) side view. For clarity, the $[PPP^+]$ gegencation and the hydrogens have been omitted. The thermal ellipsoids are drawn at the 30% probability level.

Table III. Selected Bond Distances (Å) and Angles (deg) in $[Cp^*Re(CO)_2Br][Ph_4P]$[a]

	Bond Distances		
Re–Br	2.604 (1)	Re–C(1)	1.919 (12)
Re–C(2)	1.955 (13)	Re–C(3)	2.266 (12)
Re–C(4)	2.224 (13)	Re–C(5)	2.313 (14)
Re–C(6)	2.388 (12)	Re–C(7)	2.330 (11)
P–C(11)	1.789 (11)	P–C(21)	1.803 (10)
P–C(31)	1.803 (11)	P–C(41)	1.802 (11)
O(1)–C(1)	1.11 (2)	O(2)–C(2)	1.07 (2)
C(3)–C(3′)	1.50 (2)	C(3)–C(4)	1.41 (2)
C(3)–C(7)	1.44 (2)	C(4)–C(4′)	1.55 (2)
C(4)–C(5)	1.48 (2)	C(5)–C(5′)	1.55 (2)
C(5)–C(6)	1.40 (2)	C(6)–C(6′)	1.52 (2)
C(6)–C(7)	1.42 (2)	C(7)–C(7′)	1.56 (2)
	Bond Angles		
Br–Re–C(1)	100.5 (4)	Br–Re–C(2)	94.8 (4)
Br–Re–C(3)	140.1 (3)	Br–Re–C(4)	146.1 (4)
Br–Re–C(5)	108.3 (3)	Br–Re–C(6)	89.4 (3)
Br–Re–C(7)	104.0 (3)	C(1)–Re–C(2)	90.5 (5)
C(1)–Re–C(3)	118.6 (5)	C(1)–Re–C(4)	90.4 (5)
C(1)–Re–C(5)	97.5 (5)	C(1)–Re–C(6)	130.5 (5)
C(1)–Re–C(7)	150.4 (5)	C(2)–Re–C(3)	92.4 (5)
C(2)–Re–C(4)	117.3 (5)	C(2)–Re–C(5)	153.6 (5)
C(2)–Re–C(6)	137.2 (4)	C(2)–Re–C(7)	103.4 (5)
C(3)–Re–C(4)	36.5 (5)	C(3)–Re–C(5)	61.6 (5)
C(3)–Re–C(6)	60.1 (4)	C(3)–Re–C(7)	36.4 (5)
C(4)–Re–C(5)	38.1 (5)	C(4)–Re–C(6)	60.1 (5)
C(4)–Re–C(7)	60.1 (5)	C(5)–Re–C(6)	34.7 (4)
C(5)–Re–C(7)	59.2 (4)	C(6)–Re–C(7)	35.1 (4)
Re–C(1)–O(1)	170 (1)	Re–C(2)–O(2)	175 (1)
Re–C(3)–C(3′)	125 (1)	Re–C(3)–C(4)	70.1 (7)
Re–C(3)–C(7)	74.3 (7)	C(3′)–C(3)–C(4)	127 (1)
C(3′)–C(3)–C(7)	126 (1)	C(4)–C(3)–C(7)	107 (1)
Re–C(4)–C(3)	73.4 (7)	Re–C(4)–C(4′)	126 (1)
Re–C(4)–C(5)	74.2 (8)	C(3)–C(4)–C(4′)	128 (1)
C(3)–C(4)–C(5)	109 (1)	C(4′)–C(4)–C(5)	123 (1)
Re–C(5)–C(4)	67.7 (7)	Re–C(5)–C(5′)	126 (1)
Re–C(5)–C(6)	75.6 (7)	C(4)–C(5)–C(5′)	130 (1)
C(4)–C(5)–C(6)	107 (1)	C(5′)–C(5)–C(6)	123 (1)
Re–C(6)–C(5)	69.7 (7)	Re–C(6)–C(6′)	125.7 (9)
Re–C(6)–C(7)	70.2 (7)	C(5)–C(6)–C(6′)	128 (1)
C(5)–C(6)–C(7)	109 (1)	C(6′)–C(6)–C(7)	124 (1)
Re–C(7)–C(3)	69.4 (7)	Re–C(7)–C(6)	74.7 (7)
Re–C(7)–C(7′)	128.8 (9)	C(3)–C(7)–C(6)	109 (1)
C(3)–C(7)–C(7′)	124 (1)	C(6)–C(7)–C(7′)	126 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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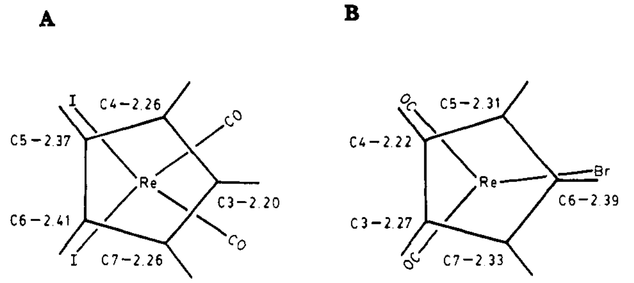

Figure 3. Top view of (A) *lat*-(η^5-C$_5$Me$_5$)Re(CO)$_2$I$_2$ and (B) [(η^5-C$_5$Me$_5$)Re(CO)$_2$Br$^-$], showing the Cp* ring–rhenium bond lengths (Å). Distances for the former complex are taken from ref 16.

plexes.[16,17,34] The C–C bonds of the Cp* ring range from 1.40 (2) to 1.48 (2) Å with an average length of 1.43 (2) Å in agreement with other peralkylated cyclopentadienylrhenium complexes.[16,17,35]

The disparate Re–C(ring) bond lengths indicate that the Cp* ring is tilted away from the bromine atom and toward the two carbonyl groups. The Re–C(6) bond is the longest at 2.388 (12) Å and is followed by the Re–C(7) and Re–C(5) lengths of 2.330 (11) and 2.313 (14) Å, respectively. The shortest Re–C(ring) distances of 2.266 (12) and 2.224 (13) Å belong to Re–C(3) and Re–C(4), respectively. These variations in the Re–C(ring) bond lengths are not entirely unexpected when the crystallographic results of *lat*-Cp*Re(CO)$_2$I$_2$ and the theoretical studies of related CpML$_4$ complexes are considered.[36] For example, in *lat*-Cp*Re(CO)$_2$I$_2$ the Re–C(ring) bonds that are pseudotrans (formally opposite) to the two carbonyl ligands are observed to be longer than the corresponding Re–C(ring) bonds that are opposite the iodide ligands, as shown in Figure 3. The bond length asymmetry in **2**$^-$ (as in *lat*-Cp*Re(CO)$_2$I$_2$) is readily rationalized in terms of the π-acceptor properties of the CO ligands. The CO ligands accept π-electron density (via the π^* manifold) from the Cp* ring at the expense of the opposite Re–C(5–7) bonds; this results in an elongation and a tilting of the Cp* ring toward the carbonyl ligands. Alternatively, Cp* ring tilting may be viewed as arising from a metal δ-orbital (d$_{xy}$)–Cp* π^*-orbital (e$_2$) interaction.[36] The Cp* ring is expected to exhibit maximum tilting in d^5-ML$_4$ fragments that possess an eclipsed conformation; small deviations from an eclipsed conformation are not expected to negate the predicted trends in Cp ring tilting.[16]

On the basis of the aforementioned expectation, the isolobal relationship predicts that **2**$^-$ should display a similar tilting pattern as in *lat*-Cp*Re(CO)$_2$I$_2$[16] and CpMo(CO)$_3$Me,[36] since the [Re(CO)$_2$Br$^-$] fragment is formally a d^7-ML$_3$ species and is equivalent to its isolobal d^5-ML$_4$ counterparts.[37] In this connection the metal fragments are derived by treating the Cp ring as a neutral five-electron donor. An alternative procedure would involve treating the Cp ring as an anionic six-electron donor with concomitant charge adjustment for the metal fragment; i.e., Re(CO)$_2$Br is isolobal with [Re(CO)$_2$I$_2^+$]. Regardless of the exact factor(s) responsible for Cp* ring tilting, the isolobal nature of these metal fragments underscores the predicted and experimentally observed similarity among **2**$^-$, *lat*-Cp*Re(CO)$_2$I$_2$, and CpMo(CO)$_3$Me.

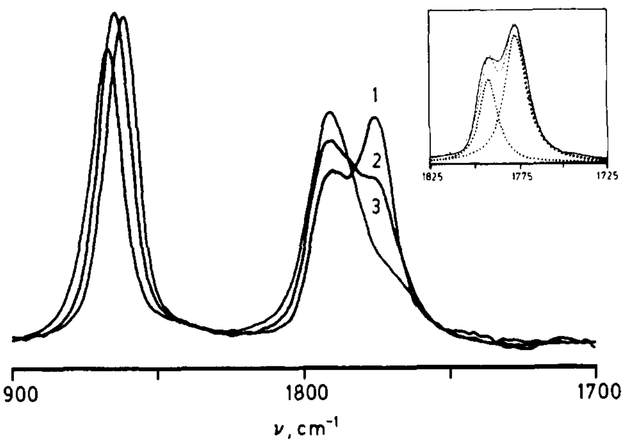

Figure 4. Infrared spectra of the carbonyl region for [(η^5-C$_5$Me$_5$)Re(CO)$_2$Br][Na] in THF as a function of temperature: (1) −70 °C; (2) −30 °C; (3) 25 °C. The inset displays the antisymmetric carbonyl region (1825–1725 cm^{-1}) for the experimental spectrum (—) of [**2**][Na] recorded at −70 °C, resolved bands (···) for the contact and solvent-separated ions, and the theoretical curve (- - -) for both ion pairs.

IV. Reduction Studies Using One-Electron Reducing Agents. The reduction of *lat*- and *diag*-**1** was next examined by using known one-electron reducing agents in order to probe for the intermediacy of the corresponding 19e$^-$ complex [Cp*Re(CO)$_2$Br$_2^{\bullet-}$]. Treatment of **1** (either isomer) in THF at −78 °C with 1 equiv of cobaltocene or potassium naphthalide immediately gave 0.5 mol equiv of **2**$^-$, as assayed by low-temperature IR analysis. Use of 2.0 equiv of reducing agent afforded **2**$^-$ in quantitative yield, as expected for a two-electron reduction process. The resulting two ν(CO) bands of the rhenium anion are identical in intensity and frequency with those of [**2**][Li] and suggest that negligible ion pairing is present between **2**$^-$ and the gegencation (vide supra). The fact that the 19e$^-$ radical anion is not observed indicates that the lifetime of [Cp*Re(CO)$_2$Br$_2^{\bullet-}$] is very short and is followed by faster subsequent reactions to ultimately give **2**$^-$. Loss of bromide from [Cp*Re(CO)$_2$Br$_2^{\bullet-}$] is anticipated to give the 17e$^-$ complex Cp*Re(CO)$_2$Br, which is then expected to accept a second electron in a fast electron transfer step involving the reducing agent.[38] Electron transfer from [Cp*Re(CO)$_2$Br$_2^{\bullet-}$] to Cp*Re(CO)$_2$Br is also expected to yield **2**$^-$ and regenerate **1**. The importance of this pathway will depend on the relative magnitude of the rates associated with bromide loss and electron transfer from the 19e$^-$ complex [Cp*Re(CO)$_2$Br$_2^{\bullet-}$]. The net outcome of these chemical reductions will still adhere to a formal two-electron reduction of **1**.

Facile loss of bromide, compared to CO loss, is also predicted when one considers the π acidity of these two ligands. Here the weaker π-acceptor ligand preferentially dissociates so as to minimize unfavorable metal–ligand orbital interactions in the 19e$^-$ radical anion.[39] Alternatively, **1**$^-$ could undergo a second electron accession to give a 20e$^-$ complex (assuming no ring hapticity changes), followed by bromide loss to give **2**$^-$. We favor the former pathway on the basis of reports of dissociative halide loss in organic halides and metal dimer fragmentation reactions upon one-electron reduction[40] and note that these two schemes have precedence in

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Table IV. Equilibrium Parameters for the Conversion of [**2**][Na] from Contact Ions into Solvent-Separated Ions[a]

$1000/T$, K^{-1}	ln k_{eq}[b]	$1000/T$, K^{-1}	ln k_{eq}[b]
3.36	0.405	3.95	−0.136
3.36	0.456[c]	4.20	−0.439
3.53	0.306	4.39	−0.571
3.60	0.261	4.59	−0.717
3.66	0.148	4.69	−0.719
3.80	0.040	4.93	−0.974
3.80	−0.012[c]		

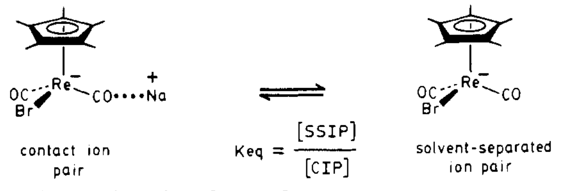
$\Delta H = 1.8 \pm 0.06$ kcal/mol;[d] $\Delta S = 7.0 \pm 0.2$ eu[d]

[a] From 2.5×10^{-3} M [Cp*Re(CO)$_2$Br][Na] in THF by following the changes in the area of the 1790 and 1776 cm^{-1} carbonyl bands. [b] Defined as the [area of solvent-separated ions]/[area of carbonyl oxygen–sodium contact ions]. [c] Multiple determination from a second separate experiment. [d] Error limits at 95% confidence limits.

electrochemistry as they formally conform to an ECE and EEC process, respectively.[41] Currently, we are examining the redox chemistry of **1** using electrochemical techniques in order to unambiguously define the point of bromide loss; the redox properties of *lat-* and *diag-***1** will be the subject of a future paper.

Treatment of **1** in THF at −78 °C with sodium naphthalide (2 mol equiv) was observed to occur rapidly to give [**2**][Na] (vide supra). However, low-temperature IR analysis revealed that **2**$^-$ exists as a 73:27 mixture of carbonyl oxygen–[Na$^+$] and solvent-separated ion pairs, respectively. The existence of the former ion pairs was easily confirmed through the addition of either 15-crown-5 or HMPA (~10 mol equiv based on Re), which immediately afforded an IR spectrum identical with that of [**2**][Li]. The ν(CO) values of [**2**][Na] are readily assigned on the basis of their frequency and response to additives, as was done for [**2**][MgX]. The two low-frequency ν(CO) bands at 1790 and 1776 cm^{-1} represent the antisymmetric carbonyl stretching mode associated with the solvent-separated and carbonyl oxygen–sodium contact ion pairs, respectively. In principle, two additional ν(CO) bands corresponding to a symmetric carbonyl stretch for each type of ion pair should be observed; however, only one band is observed at 1863 cm^{-1}. An analogous situation involving [CpFe(CO)$_2$][Na] has also been observed by Pannell and Jackson and presumably is the result of coupling and/or inadequate band resolution.[27a,42]

Having established the nature of ion pairs in solution for [**2**][Na], we next examined the effect of temperature on the equilibrium between these ion pairs in order to quantify the thermodynamics associated with this system. Figure 4 shows selected IR spectra for [**2**][Na] as a function of temperature. As the temperature is raised from −78 °C to room temperature, the equilibrium constant is gradually shifted to the solvent-separated ion pairs in accordance with the equilibrium shown in eq 3. The ion pairing exhibited by [**2**][Na] represents another example of the subtle balance between the electrostatic anion/cation interaction and the solvation of the cation by THF in determining the extent of ion pairing in organometallic complexes. Lithium and potassium ion pairing in **2**$^-$ is negligible on the basis of the formation of stable [Li$^+$]·nTHF solvates and an insufficient [K$^+$] electrostatic potential, which minimizes anion/cation interactions.[26,43] Extensive sodium ion pairing results from [Na$^+$]'s intermediate oxophilicity and electrostatic properties, which favor contact ion pairs.[26,43]



$$\mathrm{Keq} = \frac{[\mathrm{SSIP}]}{[\mathrm{CIP}]} \qquad (3)$$

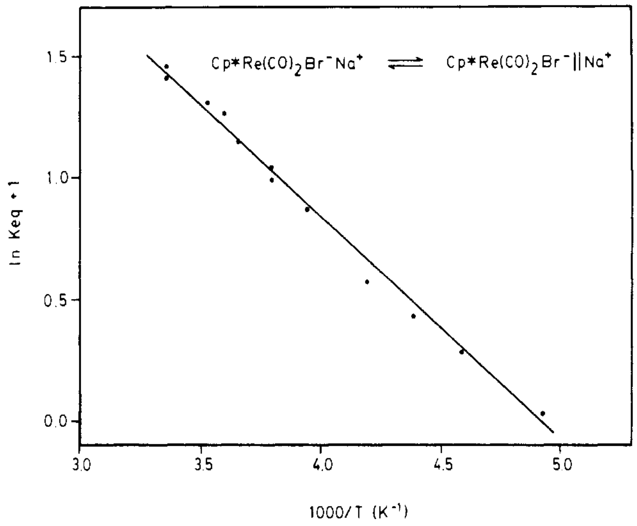


Figure 5. Plot of ln K_{eq} + 1 vs $1/T$ for the contact ⇌ solvent-separated ion pair equilibrium for [(η^5-C$_5$Me$_5$)Re(CO)$_2$Br][Na] in THF.

Band-area measurements on the two, overlapping antisymmetric carbonyl stretching bands were performed with the assumption that the area under each absorption may be taken to be proportional to the relative amount of each ion pair. Table IV gives the K_{eq} values for the equilibrium defined in eq 3 from which a Van't Hoff plot showing the variation of ln K_{eq} as a function of temperature is readily constructed (Figure 5). Values of 1.8 ± 0.06 kcal/mol for ΔH and 7.0 ± 0.2 eu for ΔS are computed from the slope of the straight line and the intercept, respectively.

It is immediately apparent that the enthalpic and entropic contribution to the ion pair equilibrium oppose each other. Low temperatures (<263 K) favor contact ion pairs as a result of an exothermic electrostatic interaction between **2**$^-$ and [Na$^+$], while higher temperatures lead to solvent-separated ion pairs as the $T\Delta S$ term dominates the free energy change associated with the equilibrium. A similar temperature-dependent process has also been reported for [Co(CO)$_4$][Na] in THF by Edgell and Lyford.[27b] In that study the ΔH and ΔS values were observed to be 3.7 kcal/mol and 14 eu, respectively, for the equilibrium defined analogously to our eq 3. Our thermodynamic values compare well with those of Edgell and Lyford and indicate that the carbonyl oxygen–sodium interaction in [Co(CO)$_4$][Na] is stronger than in [**2**][Na]. Finally, we note that the conversion of contact ion pairs of [**2**][Na] into solvent-separated ion pairs displays a temperature response that is different from several aromatic carbanions and complexes of macrocyclic polyethers. For example, Jackman et al.[44] have demonstrated that sodium fluorenide exists primarily as contact ions at room temperature (~95%), while potassium fluorenide/18-crown-6 solutions are predicted to exhibit increased ion pairing as the temperature is raised above room

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temperature.[27c] While an explanation concerning the difference in ΔH for the conversion of contact ions into solvent-separated ions has been proposed,[27b] no current theory exists that adequately explains such an inverse temperature behavior between organic and organometallic ions.

V. Reactivity and Stability Studies of $\mathbf{2}^-$. The functionalization of $\mathbf{2}^-$ was examined as a potential route to complexes of the form $Cp^*Re(CO)_2Br(R)$. Treatment of $\mathbf{2}^-$ in THF with trifluoroacetic acid afforded two new $\nu(CO)$ bands at 2018 and 1945 cm^{-1}, as expected for anion protonation. From the intensity pattern of the $\nu(CO)$ bands we conclude that protonation proceeds to give $Cp^*Re(CO)_2Br(H)$ with diagonal stereochemistry.[18] $\mathbf{2}^-$ also reacts with methyl triflate and magic ethyl in CH_2Cl_2 to yield the corresponding *diag*-$Cp^*Re(CO)_2Br(R)$ complexes on the basis of in situ IR analysis. The $\nu(CO)$ bands for *diag*-$Cp^*Re(CO)_2Br(Me)$ were observed at 2016 (s) and 1935 (s) cm^{-1}, while those for *diag*-$Cp^*Re(CO)_2Br(Et)$ appeared at 2020 (s) and 1944 (vs) cm^{-1}. All of these functionalized anions decomposed in solution over a period of days to give $Cp^*Re(CO)_3$ as the only isolable product (~20–30% isolated yield).

Finally, THF solutions of $\mathbf{2}^-$ were observed to be stable for a period of weeks when oxygen was rigorously excluded. The presence of oxygen leads to complex mixtures of rhenium oxides in addition to $Cp^*Re(CO)_3$. For example, [**2**][K] slowly decomposed in septum-capped vessels on the benchtop to give the known oxides Cp^*ReO_3[46] and $[ReO_4^-]$ as the major products. IR analysis (KBr pellet) revealed intense $\nu(Re{=}O)$ bands at 909 and 877 cm^{-1} assignable to Cp^*ReO_3 and an intense band at 913 cm^{-1} attributed to potassium perrhenate. The latter $\nu(Re{=}O)$ band observed was identical with that exhibited by pure $[ReO_4^-]$. We have also observed perrhenate formation when the analogous $[CpRe(CO)_2Br^-]$ complex is decomposed under an oxygen atmosphere.[19] The exact pathways and other products involved in this decomposition reaction remain as unanswered questions for future study.

Experimental Section

Pyridinium hydrobromide perbromide[47] and cobaltocene[48] were prepared from known literature procedures, while $Cp^*Re(CO)_3$ was prepared according to the method of Gladysz et al.[21a] MeLi (1.4 M in Et_2O), PhLi (2.0 M in C_6H_{12}), *t*-BuLi (1.7 M in pentane), MeMgBr (1.5 M in toluene/THF, 75/25), *t*-BuMgCl (2.0 M in THF), Super-H (1.0 M in THF), and K-Selectride (1.0 M in THF) were all purchased from Aldrich and used as received. Magic ethyl was obtained from Alpha and transferred to a Schlenk vessel for storage while methyl triflate was prepared according to the published procedure.[49] All reactions were conducted under argon with Schlenk techniques[50] or in a nitrogen-filled Vacuum Atmosphere DL series inert-atmosphere Dri-box. THF and heptane were distilled from sodium/benzophenone ketyl and stored under argon in Schlenk vessels. HMPA was distilled from CaH_2, while CD_2Cl_2 and $CDCl_3$ were distilled from P_2O_5 and stored under argon in Schlenk vessels. The C and H analysis was performed by Atlantic Microlab, Atlanta, GA.

Routine infrared spectra were recorded on a Nicolet 20SXB FT-IR spectrometer in 0.1-mm NaCl cells. Low-temperature IR spectra were recorded on the same spectrometer with a Specac Model P/N 21.000 variable-temperature cell equipped with inner and outer CaF_2 windows. Dry ice/acetone was used as coolant, and the reported cell temperatures, taken to be accurate to ±1 °C, were determined with a copper–constantan thermocouple. ^1H NMR spectra were recorded at 300 or 90 MHz on Varian 300-VXR and JEOL FX-90Q spectrometers, respectively. ^{13}C NMR spectra were obtained at 75 MHz by using the former spectrometer.

Preparation of *lat*- and *diag*-$Cp^*Re(CO)_2Br_2$. To 9.7 g (24 mmol) of $Cp^*Re(CO)_3$ and 8.0 g (25 mmol) of pyridinium hydrobromide perbromide in a 500-mL Schlenk flask was added ca. 70 mL of TFA. The mixture was stirred for 1 h and then poured into 1 L of water. The resulting light brown precipitate was collected on a medium-porosity frit and washed with several portions of water. The filtered precipitate was redissolved in CH_2Cl_2 (~250 mL) and the solution dried overnight with $CaCl_2$. The pure dibromides were subsequently isolated by column chromatography over silica gel using petroleum ether/CH_2Cl_2 (1:1) and displayed spectral properties (IR and NMR) identical with those reported by Sutton et al.[16] Yield: *lat*-**1**, 4.7 g (36.6%); *diag*-**1**, 0.5 g (3.9%). Note: use of Br_2 directly and/or longer reaction times led to an overall decrease in the yield of the isomeric dibromides.

Preparation of [$Cp^*Re(CO)_2Br$][PPP]. To 0.2 g (0.37 mmol) of *lat*-**1** in THF (~35 mL) at −78 °C was added 0.23 mL (0.39 mmol) of a 1.7 M *t*-BuLi solution. The solution was allowed to warm to room temperature and was then treated with 0.14 g (0.37 mmol) of [PPP][Cl]. The solution was concentrated to ~10 mL, filtered under argon by using a fine-porosity frit, and then layered with ~10 mL of heptane. The analytical sample and crystals suitable for X-ray diffraction analysis were obtained after 2 days at room temperature. Yield: 0.25 g (84.8%) of [**2**][PPP]. IR (CH_2Cl_2): $\nu(CO)$ 1860 (s), 1781 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.94 (15 H, methyls), 7.75 (20 H, aromatics). ^{13}C NMR (CD_2Cl_2): δ 11.0 (5 C, methyls), 93.8 (5 C, Cp* ring), 117.9 (1 C, quaternary C, J_{P-C} = 90 Hz), 131.0 and 134.8 (2 C each, ortho and meta), 136.1 (1 C, para), 213.1 (2 C, CO's). Anal. Calcd for $C_{36}H_{35}BrO_2PRe$: C, 54.28; H, 4.40. Found: C, 54.32; H, 4.43.

Reaction of 1 with One-Electron Reducing Agents. In a typical experiment, 26.9 mg (0.05 mmol) of **1** (either isomer) in 20 mL of THF at −78 °C was treated with 0.2 mL of a 0.5 M sodium naphthalide solution. The reaction was instantaneous, as judged by the immediate discharge of the red solution of **1** to that of yellow $\mathbf{2}^-$. The [**2**][Na] prepared in this manner (~2.5×10^{-3} M in Re) was also used in the ion-pairing equilibrium study after cannulation into the variable-temperature IR cell.

Reaction of [2][Li] with TFA. To 50.0 mg (0.1 mmol) of [**2**][Li] (prepared from *lat*-**1** and *t*-BuLi) in 50 mL of THF at −78 °C was added 0.1 mL (excess) TFA. The solution was allowed to warm to room temperature and examined by IR ($\nu(CO)$ for *diag*-$Cp^*Re(CO)_2Br(H)$: 2018 (s) and 1945 (vs) cm^{-1}). The solution gradually acquired a dark brown color and displayed only the presence of $Cp^*Re(CO)_3$ after several days. $Cp^*Re(CO)_3$ was isolated (25% yield) by column chromatography and verified by comparison to an authentic sample of $Cp^*Re(CO)_3$. The reactions of [**2**][Li] with methyl triflate and magic ethyl were conducted similarly. The expected alkylation product exhibited only diagonal stereochemistry by IR analysis and was observed to decompose over the course of days (usually 1–3 days) to give only $Cp^*Re(CO)_3$, as judged by IR spectroscopy.

The protonation reaction was also examined by ^1H NMR spectroscopy using [**2**][PPP]. Here 25.0 mg of [**2**][PPP] was added to a 5-mm NMR tube inside the Dri-box after which 0.5 mL of $CDCl_3$ and 0.05 mL (excess) of TFA were added. The tube was freeze–pump–thaw degassed three times prior to flame sealing. ^1H NMR analysis exhibited resonances at δ 2.01 (15 H, methyls) and −9.98 (1 H, hydride). Decomposition of *diag*-$Cp^*Re(CO)_2Br(H)$ was evident after 6 h at room temperature.

Crystallographic Analysis. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 24 ± 2 °C by using graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. An empirical absorption was applied. The structure was solved by MULTAN,[51] and successive cycles of difference Fourier syntheses were followed by least-squares refinement. Data with intensities less than $3\sigma(I)$ were rejected, and a non-Poisson contribution weighting scheme with an intensity factor P set at 0.04 was used in the final stages of refinement.[52]

Crystals of [**2**][PPP] were grown from a solution of THF and heptane (vide supra). A suitable yellow prism was mounted in a thin-walled glass capillary and sealed under nitrogen. All non-hydrogen atoms were refined anisotropically, and scattering factors were taken from ref 53.

Band-Shape Analysis. Since the antisymmetric carbonyl stretching bands of the sodium-contact and solvent-separated ion pairs exhibit sig-

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nificant overlap, the infrared band shapes of these CO bands were calculated by using a numerical procedure in order to determine the ratio of their areas. Absorbances were digitized from 1825 to 1725 cm^{-1} at 2-cm^{-1} intervals and entered into files on the university VAX 11/85 computer. Following base-line correction, the spectra were fit by a model consisting of Lorentzian band shapes, each characterized by a peak frequency (ν), maximum intensity (I), and half-width (fwhh) (Δ). Since the instrument resolution (2 cm^{-1}) is far less than the observed bandwidths (~20 cm^{-1}), it was unnecessary to convolute the model spectrum with a resolution (slit) function. The parameters were varied to minimize the squared deviation between the experimental and calculated intensities by using a standard nonlinear regression procedure.[54] A representative experimental and calculated spectrum of [**2**][Na] at −70 °C is shown in Figure 4. Given that the area of a Lorentzian peak is proportional to the product of the bandwidth and the maximum intensity, the area ratio of the different ion pairs is calculated easily as $A_2/A_1 = (I_2\Delta_2)/(I_1\Delta_1)$.

Thermodynamic Evaluation of the Ion-Pairing Equilibrium in [2][Na]. THF solutions 2.5 × 10^{-3} M in [**2**][Na] (vide supra) were used to measure the amount of contact and solvent-separated ion pairs in solution over the temperature range of −70 °C to room temperature. From the area associated with each antisymmetric carbonyl stretching band, the equilibrium constants were easily determined as defined by eq 3. The thermodynamic parameters were obtained by plotting ln K_{eq} vs T^{-1}, from which the slope and intercept afforded ΔH and ΔS, respectively. The error limits associated with the enthalpy and entropy for ion pairing were calculated by using the available least-squares regression program[55] and should not be taken to reflect uncertainties in sample preparation, band-area intensities, or temperature control but rather the deviation of the data points about the least-squares line.

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Supplementary Material Available: An ORTEP view of the [PPP^+] cation and a table of anisotropic thermal parameters (3 pages); a listing of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of Layered Calcium and Lanthanide Phosphonate Salts

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The crystal structures of two layered calcium phosphonate salts, $Ca(O_3PCH_3)\cdot H_2O$ and $Ca(HO_3PC_6H_{13})_2$, were solved by single-crystal X-ray diffraction. $Ca(O_3PCH_3)\cdot H_2O$ is monoclinic, space group $P2_1/c$, with $Z = 4$, $a = 8.8562$ (13) Å, $b = 6.6961$ (10) Å, $c = 8.1020$ (10) Å, $\beta = 96.910$ (11)°, and $V = 476.97$ (12) Å^3. Ca atoms are coordinated by six oxygen atoms at a distance of ca. 2.4 Å, and by a seventh at 2.7 Å, making the coordination environment a distorted pentagonal bipyramid. In this salt, and in the structurally related $M(O_3PC_nH_{2n+1})\cdot H_2O$ ($n \leq 5$; M = Ca, Cd) series, the metal–phosphonate coordination is 5:5. $Ca(HO_3PC_6H_{13})_2$ is triclinic, space group $P\bar{1}$, with $Z = 2$, $a = 5.606$ (2) Å, $b = 7.343$ (3) Å, $c = 21.158$ (7) Å, $\alpha = 97.31$ (3)°, $\beta = 96.98$ (3)°, $\gamma = 90.43$ (4)°, and $V = 857.2$ (6) Å^3. In this structure and the related $Ca(HO_3PC_nH_{2n+1})_2$ ($6 < n < 18$) series, the Ca atoms lie in approximately coplanar sheets and are coordinated by six oxygen atoms from different phosphonate groups lying above and below the plane. This structure is closely related to that of α-$Zr(HPO_4)_2\cdot H_2O$ and the tetravalent metal phosphonates $M(O_3PR)_2$ (M = Zr, Hf, Ti, Ce). Layered trivalent metal phosphonate salts $MH(O_3PR)_2$ (R = alkyl, phenyl; M = La, Sm, Ce) were also prepared. $LaH(O_3PCH_3)_2$ is triclinic with $Z = 2$, $a = 5.398$ (7) Å, $b = 8.168$ (18) Å, $c = 10.162$ (19) Å, $\alpha = 73.76$ (16)°, $\beta = 83.89$ (13)°, $\gamma = 73.50$ (14)°, and $V = 412.3$ (13) Å^3. The structure of the $MH(O_3PR)_2$ compounds appears to be closely related to that of the other 1:2 layered metal phosphonate salts $Ca(HO_3PC_nH_{2n+1})_2$ and $M(O_3PR)_2$.

Introduction

There has been considerable interest in the synthesis of new layered metal phosphonate salts,[1-6] because these materials have robust yet flexible structures. They are hybrid organic/inorganic materials in which the structure is directed by the choice of metal and reaction conditions and the nature of the interlayer region depends on the organic moiety. Since pillared[3] and intercalated[3,6] structures can be easily generated, they have been extensively investigated as catalysts, sorbents, and ion exchangers.

Frequently the structures of new metal phosphonates (which are often difficult to prepare as single crystals) can be related to those of known inorganic or mineral phosphates. For example, the structures of the tetravalent metal phosphonates $M(O_3PR)_2$ (M = Zr, Ti, Hf, Ce, Th) are believed[3-6] to be closely related to that of α-zirconium phosphate, $Zr(O_3POH)_2\cdot H_2O$, which was solved in 1969 by Clearfield and Smith.[7] Likewise, the vanadyl phosphonates $VO(RPO_3)\cdot H_2O\cdot R'OH$ described by Johnson and Co-workers[8] appear to be derived from the newberyite, $Mg(O_3POH)\cdot 3H_2O$, structure.[9]

Recently, we demonstrated that insoluble tetravalent and trivalent metal phosphonates, $M(O_3PR)_2$ and $MH(O_3PR)_2$, could

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