Synthesis and reactions of aminooxy carbene complexes of rhenium

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Abstract

The reaction of $Re(CO)_5Br$ and $\overline{HNCH_2CH_2}$, in the presence of Br^-, gives the aminooxycarbene complex *cis*-$Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ (I) at room temperature, but *fac*-$Re(CO)_3(Br)(=\overline{COCH_2CH_2NH})_2$ (II) is obtained in refluxing CH_3CN. Refluxing I with PPh_3 in toluene gives *fac*-$Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2}$ $\overline{CH_2NH})$ (III). Both I and III are deprotonated by n-BuLi to give the imine complexes, $Re(CO)_4(Br)(\overline{C=NCH_2CH_2O})^-Li^+$ and $Re(CO)_3(PPh_3)(Br)(-\overline{C=}$ $\overline{NCH_2CH_2O})^-Li^+$, respectively, whose nitrogen atoms are methylated with Me_3O^+ to yield the *N*-methyl carbenes, $Re(CO)_4(Br)(=\overline{COCH_2CH_2NMe})$ (V) and $Re(CO)_3(Br)(PPh_3)(=\overline{COCH_2CH_2NMe})$ (IV). The reaction of V with MeLi yields $Re(CO)_4(=\overline{COCH_2CH_2NMe})^-Li^+$ which then reacts with MeI to generate the carbene alkyl compound $Re(CO)_4(CH_3)(=\overline{COCH_2CH_2NMe})$ (VI). Upon reaction with potassium hydrotris(1-pyrazolyl)borate, $KHB(pz)_3$, I yields *fac*-$[\eta^2\text{-}HB(pz)_3]$ $Re(CO)_3(=\overline{COCH_2CH_2NH})$ (VII), in which the $HB(pz)_3$ is only bidentate. Under UV photolysis VII loses a CO thereby allowing the third pyrazolyl group to coordinate in $[\eta^3\text{-}HB(pz)_3]Re(CO)_2(=\overline{COCH_2CH_2NH})$ (VIII). All of the new compounds are characterized by their IR, ^1H NMR, and ^{13}C NMR spectra.

Introduction

Our group has reported the synthesis of a number of transition metal complexes containing cyclic dioxy-, aminooxy-, aminothio-, and dithio-carbene ligands [1–4]. The aminooxycarbene complexes were produced by the halide-catalyzed reaction of transition metal carbonyls with aziridine according to eq. 1.

$$M \equiv C \equiv O \ + \ \overline{HNCH_2CH_2} \ \xrightarrow{X^-} \ M = C \diagup^{O}_{\diagdown N-} \qquad (1)$$
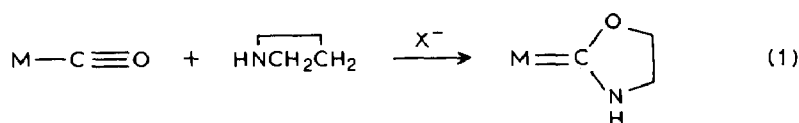
$(M = Fe(CO)_4, Re(CO)_4X \ (X = Cl, Br, I), Mn(CO)_4X \ (X = Cl, Br, I), CpFe(CO)_2^+,$

$CpMn(CO)(NO)^+, CpRu(CO)_2^+, \text{ and } CpFe(PPh_3)(CO)^+)$

In the present paper, we report further studies of the aminooxycarbene complex, $Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ (I) in which CO is replaced by phosphine or hydrotris(pyrazolyl)borate ligands, the Br is replaced by CH_3, and the H on the carbene N is replaced by CH_3.

Experimental

General procedures

All reactions and manipulations were performed using standard Schlenk techniques under prepurified N_2. Unless noted otherwise, reagent grade chemicals were used without further purification. Methylene chloride, hexanes and acetonitrile were distilled from CaH_2 and stored under N_2 over type 4Å molecular sieves. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under N_2.

The starting compounds $Re(CO)_5Br$ [5] and $Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ (I) [2] were prepared as reported in the literature. Aziridine [6] $(\overline{CH_2CH_2NH})$ was distilled and stored over KOH before use. Schlenk flasks used in reactions of n-BuLi or CH_3Li were dried in an oven at $120\,^\circ C$ overnight prior to use and then cooled in a dessicator flushed with N_2 [7].

Infrared spectra were recorded on a Perkin–Elmer 681 instrument. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Nicolet 300 MHz spectrometer at room temperature. $Cr(acac)_3$ was added to the solutions to reduce ^{13}C NMR data collection times. Melting points (uncorrected) of the compounds were determined in air on a Thomas Hoover capillary melting-point apparatus. Electron impact mass spectra were obtained using a Finnigan 4000/GC–MS. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

fac-Re(CO)$_3$(Br)(=$\overline{COCH_2CH_2NH}$)$_2$ (II)

To a mixture of 0.50 g (1.2 mmol) of $Re(CO)_5Br$ and 0.51 g (2.5 mmol) of $BrCH_2CH_2NH_2 \cdot HBr$ in 20 ml of CH_3CN was added 0.16 ml (3.1 mmol) of aziridine. After being refluxed under N_2 for 5 h, the reaction was complete according to the IR spectrum. The reaction mixture was taken to dryness under vacuum. The yellow residue was dissolved in 20 ml of CH_2Cl_2. After filtering through anhydrous $MgSO_4$, the CH_2Cl_2 solution was concentrated and 30 ml of hexanes was added. It was stored at $-20\,^\circ C$ overnight to generate yellow microcrystals. Yield: 0.46 g (76%). M.p. 124–127°C. Anal. Found: C, 21.92; H, 1.94; N, 5.48. $C_9H_{10}BrN_2O_5Re$ calcd.: C, 21.95; H, 2.03; N, 5.69%. Mass spectrum: m/e (rel. intensity, probable assignment): 491.9 (3.6, M^+); 463.9 (3.56, $(M-CO)^+$); 435.9 (7.24, $(M-2CO)^+$); 408.0 (1.48, $(M-3CO)^+$); 336.9 (14.2, $Re(Br)(\overline{COCH_2CH_2NH})^+$); 308.9 (16.4, $Re(Br)(CH_2CH_2NH)^+$); 71.0 (100, $COCH_2CH_2NH^+$).

fac-Re(CO)$_3$(PPh$_3$)(Br)(=$\overline{COCH_2CH_2NH}$) (III)

A mixture of PPh_3 (0.087 g, 0.33 mmol) and I (0.15 g, 0.33 mmol) in 20 ml of toluene was refluxed under N_2 for 15 min. The solvent was removed under vacuum. The colorless residue was extracted with CH_2Cl_2, and hexanes were added until a cloudy solution was observed. The solution was stored overnight at $-20\,^\circ C$ to give white crystals. Yield: 0.22 g (96%). M.p. 193°C (decomp.). Anal. Found: C, 42.03;

H, 3.14; N, 2.08. $C_{24}H_{20}BrNO_4PRe$ calcd.: C, 42.16; H, 2.93; N, 2.05%. Mass spectrum: m/e (rel. intensity, probable assignment): 683.0 (7.9, M^+); 654.8 (17.1, $(M - CO)^+$); 626.7 (29.0, $(M - 2CO)^+$); 598.7 (30.6, $(M - 3CO)^+$); 527.6 (5.9, $Re(PPh_3)(Br)^+$); 262 (100, PPh_3).

fac-Re(CO)₃(PPh₃)(Br)[=COCH₂CH₂N(CH₃)] (IV)

A slight excess of n-BuLi (0.30 ml of 2.4 M n-BuLi in hexane, 0.72 mmol) was injected into a solution of 0.46 g (0.68 mmol) of $Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2}$ $\overline{CH_2NH})$ (III) in 50 ml of freshly distilled THF at $-78°C$ to generate the deprotonated imine complex, $Re(CO)_3(PPh_3)(Br)(-\overline{C=NCH_2CH_2O})^-$ Li^+. At $-78°C$, 0.15 g (0.72 mmol) of Me_3O^+ PF_6^- was added to the yellow solution. After stirring for 5 h at room temperature, the mixture was filtered through anhydrous $MgSO_4$, and then the solvent was removed under vacuum. The yellow residue was chromatographed on a silica gel column (2.5×15 cm) using CH_2Cl_2 as the eluent to give a colorless solution. The solvent was removed under vacuum. Colorless crystals of the product were obtained from CH_2Cl_2/hexanes at $-20°C$. Yield; 0.37 g (78%). M.p. 97–99°C. Anal. Found: C, 42.19; H, 3.14; N, 1.75. $C_{25}H_{22}BrNO_4PRe \cdot 0.1\ CH_2Cl_2$ calcd.: C, 42.66; H, 3.12; N, 1.98%. Mass spectrum: m/e (rel. intensity, probable assignment): 696.9 (2.0, M^+); 668.9 (6.0, $(M - CO)^+$); 641.0 (8.0, $(M - 2CO)^+$); 612.9 (2.0, $(M - 3CO)^+$); 434.9 (17, $Re(CO)_3(Br)$ $(=\overline{COCH_2CH_2}NMe)^+$); 406.9 (32, $Re(CO)_2(Br)(=\overline{COCH_2CH_2}NMe)^+$); 262.1 (100, PPh_3).

cis-Re(CO)₄(Br)[=COCH₂CH₂N(CH₃)] (V)

One equivalent of n-BuLi (0.30 ml, 2.4 M of n-BuLi in hexanes, 0.72 mmol) was injected into a 50 ml THF solution of 0.32 g (0.72 mmol) of $Re(CO)_4(Br)(=\overline{COCH_2}$- $\overline{CH_2NH})$ at $-78°C$. Keeping the temperature at $-78°C$, 0.15 g (0.72 mmol) of Me_3O^+ PF_6^- was added. After the solution was allowed to reach room temperature, it was stirred for 2 h. The pale yellow solution was taken to dryness, and the residue was chromatographed on a silica gel column (2.5×16 cm). The first band (pale yellow) which was eluted with 1/1 CH_2Cl_2/hexanes gave a minor product which was possibly $Re(CO)_4(CH_3)(=\overline{COCH_2CH_2}NH)$. The second band (pale yellow) eluted with 2/1 CH_2Cl_2/hexanes and contained compound V. The latter solution was evaporated under vacuum to yield a pale yellow powder, which was recrystallized from CH_2Cl_2/hexanes at $-20°C$ to give pale yellow crystals of $Re(CO)_4(Br)[=\overline{COCH_2CH_2}N(CH_3)]$. Yield: 0.10 g (32%). M.p. 129–132°C. Anal. Found: C, 20.87; H, 1.60; N, 2.99. $C_8H_7BrNO_5Re$ calcd.; C, 20.73; H, 1.51; N, 3.02%. Mass spectrum: m/e (rel. intensity, probable assignment): 462.9 (79.4, M^+); 434.9 (70.3, $(M - CO)^+$); 406.9 (100, $(M - 2CO)^+$); 378.9 (14.4, $(M - 3CO)^+$); 350.9 (3.71, $(M - 4CO)^+$), 323.0 (5.52, $Re(Br)(CH_2CH_2NMe)^+$).

cis-Re(CO)₄(CH₃)[=COCH₂CH₂N(CH₃)] (VI)

A slight excess of CH_3Li (0.20 ml of 1.4 M CH_3Li in Et_2O, 0.28 mmol) was injected into a 30 ml THF solution of $Re(CO)_4(Br)[=\overline{COCH_2CH_2}N(CH_3)]$ (V) (0.13 g, 0.27 mmol) at $-78°C$, and then excess CH_3I (0.10 ml, 1.6 mmol) was added. After being stirred at room temperature for 5 h, the mixture was taken to dryness under vacuum at $0°C$ because of the high volatility of the product. The yellow oily residue was chromatographed on a silica gel column (2.5×10 cm). The

colorless band was eluted with 1/1 CH_2Cl_2/hexanes, and the solution was evaporated under vacuum at $0°C$ to generate pure white solid VI. Yield: 0.070 g (64%). M.p. 119–120°C. Anal. Found: C, 27.31; H, 2.80; N, 3.38. $C_9H_{10}NO_5Re$ calcd.: C, 27.12; H, 2.51; N, 3.52%. Mass spectrum: m/e (rel. intensity, probable assignment): 399.0 (22.2, M^+); 384.0 (100, $(M - CH_3)^+$); 356 (73.5, $(M - CH_3 - CO)^+$); 328 (51.5, $(M - CH_3 - 2CO)^+$); 313.0 (52.3, $Re(CO)_2(=\overline{COCH_2CH_2N})^+$); 300.0 (22.9, $(M - CH_3 - 3CO)^+$); 272.0 (6.11, $(M - CH_3 - 4CO)^+$).

fac-[η^2-HB(pz)$_3$]Re(CO)$_3$(=$\overline{COCH_2CH_2NH}$) (VII)

A solution of 0.090 g (0.34 mmol) of potassium hydrotris(pyrazolyl)borate, KHB(pz)$_3$, and 0.15 g (0.34 mmol) of $Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ (I) in 40 ml of THF was refluxed and stirred under N_2 for 18 h. A colorless solution and white precipitate were obtained. The mixture was filtered through anhydrous $MgSO_4$, and the solvent was removed under vacuum. The white residue was recrystallized from CH_2Cl_2/hexanes at $-20°C$. Colorless crystals were obtained. Yield: 0.10 g (55%). Anal. Found: C, 32.63; H, 3.00; N, 17.58. $C_{15}H_{15}BN_7O_4Re$ calcd.: C, 32.49; H, 2.71; N, 17.69%. Mass spectrum: (No parent ion (M^+) peak was observed at 555 (for the most intense peak which contains ^{11}B and ^{187}Re isotopes), but it did show peaks due to its fragments.) m/e (rel. intensity, probable assignment): 527.4 (12.8, $(M - CO)^+$); 499.4 (1.9, $(M - 2CO)^+$); 484.3 (26.3, $(M - CH_2CH_2NH)^+$); 400.3 (33.9, $HB(pz)_3Re^+$); 68.0 (100, $C_3H_4N_2^=$).

[η^3-HB(pz)$_3$]Re(CO)$_2$(=$\overline{COCH_2CH_2NH}$) (VIII)

A solution of 0.26 g (0.47 mmol) of [η^2-HB(pz)$_3$]Re(CO)$_3$(=$\overline{COCH_2CH_2NH}$) in 35 ml of THF was photolyzed in a quartz tube at λ 254 nm for 18 h when the reaction was complete (IR evidence). A pale brown solution was obtained. The solvent was removed under vacuum and the residue was chromatographed on a silica gel column (2.5 × x10 cm). A pale yellow band containing the product was eluted with 2/1 CH_2Cl_2/hexanes. The solution was taken to dryness. Pale yellow microcrystals were obtained by recrystallization from CH_2Cl_2/hexanes at $-20°C$. Yield: 0.060 g (23%). M.p. 202°C (decomp.). Anal. Found: C, 31.58; H, 2.83; N, 18.07. $C_{14}H_{15}BN_7O_3Re \cdot 0.06 CH_2Cl_2$ calcd.: C, 31.77; H, 2.85; N, 18.45%. Mass spectrum: m/e (rel. intensity, probable assignment): 527.1 (100, M^+); 499.1 (5.85, $(M - CO)^+$); 456.0 (5.11, $HB(pz)_3Re(CO)_2^+$); 443.1 (26.6, $(M - 3CO)^+$); 415.1 (31.8, $HB(pz)_3Re(NH)^+$); 400.1 (36.1, $HB(pz)_3Re^+$).

Results and discussion

The aminooxycarbene complex cis-$Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ (I) was prepared previously [2] by reaction of $Re(CO)_5Br$ with aziridine and $BrCH_2CH_2NH_3^+$ Br^- in CH_3CN at room temperature for 15 min (eq. 1). We now find that refluxing this mixture for 5 h with additional aziridine yields (76%) the bis(carbene) complex, II, eq. 2. It seems that both aziridine and $BrCH_2CH_2NH_3^+$ Br^- are required in
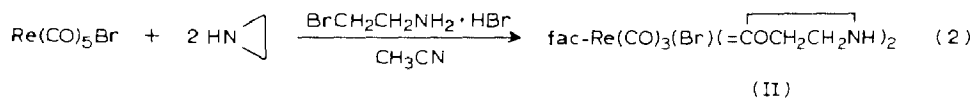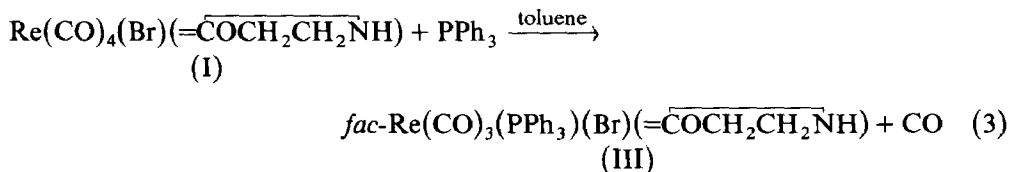
$$Re(CO)_5Br + 2 HN\!\!\triangleleft \xrightarrow[\text{CH}_3\text{CN}]{\text{BrCH}_2\text{CH}_2\text{NH}_2 \cdot \text{HBr}} fac\text{-}Re(CO)_3(Br)(=\overline{COCH_2CH_2NH})_2 \quad (2)$$

(II)

Table 1

IR data for the complexes in CH_2Cl_2 solvent

Complex	IR: $\nu(CO)$ (cm^{-1})
cis-$Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ (I)	2115m, 2009vs, 1941s
fac-$Re(CO)_3(Br)(=\overline{COCH_2CH_2NH})_2$ (II)	2040vs, 1939s, 1904s
fac-$Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2CH_2NH})$ (III)	2039vs, 1946s, 1905s
fac-$Re(CO)_3(PPh_3)(Br)[=\overline{COCH_2CH_2N}(CH_3)]$ (IV)	2038vs, 1943s, 1904s
cis-$Re(CO)_4(Br)[=\overline{COCH_2CH_2N}(CH_3)]$ (V)	2113m, 2015s, 1999s, 1940s
cis-$Re(CO)_4(CH_3)[=\overline{COCH_2CH_2N}(CH_3)]$ (VI)	2079m, 1975s, 1964s, 1915s
fac-$[\eta^2$-$HB(pz)_3]Re(CO)_3(=\overline{COCH_2CH_2NH})$ (VII)	2033s, 1930s, 1894s
$[\eta^3$-$HB(pz)_3]Re(CO)_2(=\overline{COCH_2CH_2NH})$ (VIII)	1923s, 1829s

order to obtain maximum yields of I or II from the reaction. If the reaction is performed by generating aziridine in situ from $BrCH_2CH_2NH_3^+$ Br^- and NaH (2 equiv.), some $Re(CO)_5Br$ remains unreacted even after stirring for 4 days in CH_3CN at room temperature. When this reaction is carried out in refluxing CH_3CN for 30 min, all of the $Re(CO)_5Br$ reacts to give a mixture of I and II. IR spectra taken during the reaction in eq. 2 show the presence of $Re(CO)_4(Br)(=\overline{COCH_2CH_2NH})$ (I) as an intermediate which converts to the biscarbene compound, II, by further reaction with $HN\overline{CH_2CH_2}$. The 3 nearly equally-intense $\nu(CO)$ absorptions in the IR spectrum of II (Table 1) indicate a facial geometry for II. A similar biscarbene complex, $Mn(CO)_3(Br)(=\overline{COCH_2CH_2NH})_2$, has been synthesized from $Mn(CO)_5Br$ and two equivalents of $CNCH_2CH_2OH$ in Et_2O at room temperature for 1 d [8]. The IR spectrum of $Mn(CO)_3(Br)(=\overline{COCH_2CH_2NH})_2$ $(\nu(CO)(KBr)$ 2018 vs, 1932 vs, 1905 sh, 1898 vs $cm^{-1})$ is similar to that of compound II (Table 1).

The reaction (eq. 3) of I with an equimolar amount of PPh_3 in refluxing toluene

$$Re(CO)_4(Br)(=\overline{COCH_2CH_2NH}) + PPh_3 \xrightarrow{\text{toluene}}$$
$$\text{(I)}$$

$$fac\text{-}Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2CH_2NH}) + CO \quad (3)$$
$$\text{(III)}$$

gives fac-$Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2CH_2NH})$ (II) in 96% yield within 15 min. As for II, the 3 $\nu(CO)$ bands in the IR spectrum (Table 1) of III indicate that it also has a facial structure; the spectrum is also very similar to that of the previously reported fac-$Re(CO)_3(PPh_3)(Br)(=\overline{COCH_2CH_2O})$ (2038s, 1958s, 1906s cm^{-1}) [9]. The similarity of the $\nu(CO)$ frequencies for II and III suggest that the $=\overline{COCH_2CH_2NH}$ and PPh_3 ligands have comparable electronic properties, as has been noted previously [10]. The asymmetric Re center in III causes the protons in the carbene ligand to be diastereotopic and give an ABCD pattern in the ^1H NMR spectrum; thus, four multiplets are observed at 2.88, 3.40, 3.94, 4.44 ppm (Table 2). In the ^{13}C NMR spectrum of III (Table 3) the doublet $(^2J(PC)$ 60.1 Hz) at 189.19 ppm is assigned to the CO trans to PPh_3, and the other two doublets at 194.59 and 189.31 ppm with coupling constants of 8.60 and 7.39 Hz are assigned to the CO ligands cis to the PPh_3. In other Re^I complexes, $Re(CO)_4(dppe)^+$, $Re(CO)_3(dppe)[=C(OEt)(SiPh_3)]^+$

Table 2

^{1}H NMR data for the complexes in CDCl$_3$ solvent at room temperature ^{a}

Complex	NCH$_2$	OCH$_2$	NH	Others
I	3.80 (t) ^{b}	4.77 (t) ^{b}	9.05 (br)	
II	3.77 (m)	4.66 (m)	8.93 (br)	
III	3.40 (m)	4.44 (m)	8.63 (br)	7.66 (m), 7.39(m) (PPh$_3$)
	2.88 (m)	3.94 (m)		
IV	3.34 (m)	4.18 (m)		3.69 (s) (NCH$_3$)
	3.18 (m)	3.52 (m)		7.60 (m), 7.39 (m) (PPh$_3$)
V	3.81 (t) ^{c}	4.65 (t) ^{c}		3.58 (s) (NCH$_3$)
VI	3.70 (t) ^{d}	4.56 (t) ^{d}		−0.46 (s) (ReCH$_3$)
				3.39 (s) (NCH$_3$)
VII ^{i}	3.68 (m)	4.57 (m)	9.26 (br)	7.36 (m) (H(3) and H(5) of pz)
				6.18 (m) (H(4) of pz)
VIII ^{i}	3.72 (t) ^{e}	4.50 (t) ^{e}	8.16 (br)	7.80 (d, 1H) ^{f}, 7.67 (d, 2H) ^{f}
				(H(3) of pz); 6.19 (t, 3H) ^{g}
				(H(4) of pz); 7.77 (d, 2H) ^{h}, 7.74
				(d, 1H) ^{h} (H(5)) of pz)

^{a} Chemical shifts in δ (relative to Si(CH$_3$)$_4$) and coupling constants in Hz. ^{b} J 9.77 Hz. ^{c} J 9.89 Hz. ^{d} J 9.74 Hz. ^{e} J 9.06 Hz. ^{f} J 1.47 Hz. ^{g} J 2.06 Hz. ^{h} J 2.22 Hz. ^{i} acetone-d_6 solvent.

and Re(CO)$_3$(dppe)(COSiPh$_3$). ^{13}CO coupling constants to *cis*- and *trans*-phosphines are 6–9 and 40–60 Hz, respectively [11].

The neutral imine complex, CpFe(CO)$_2$(C=NCH$_2$CH$_2$O), can be produced by deprotonation of the aminooxycarbene, CpFe(CO)$_2$(=COCH$_2$CH$_2$NH)$^+$ BF$_4^-$, in CH$_2$Cl$_2$ by K$_2$CO$_3$ or NaH [10]; this imine complex reacts with electrophiles (E$^+$) [12] (e.g., Me$_3$O$^+$ PF$_6^-$ or allyl bromide) yielding the *N*-alkyl carbene compounds (eq. 4). Similarly, the diaminocarbene *trans*-{(PPh$_3$)$_2$Pt[CN(*p*-MeC$_6$H$_4$)CH$_2$CH$_2$N-(H)]Br}BF$_4$ reacts with n-BuLi at −8°C to give the intermediate imino complex

$$[M=\overline{COCH_2CH_2NH}]^+ \xrightarrow[-HB^+]{:B} M\overline{C=NCH_2CH_2O} \xrightarrow{E^+} [M=\overline{COCH_2CH_2NE}]^+$$

(4)
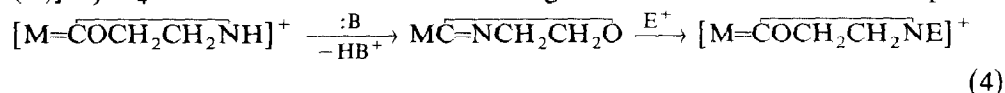
trans-{(PPh$_3$)$_2$Pt[CN(*p*-MeC$_6$H$_4$)CH$_2$CH$_2$N]Br} which rapidly reacts with allyl bromide or propargyl bromide to afford the corresponding N-substituted products [13]. Attempts to deprotonate the carbene nitrogen atoms in Re(CO)$_4$(Br)-(=COCH$_2$CH$_2$NH) (I) with the bases, NaH, LiAlH$_4$, NaN(SiMe$_3$)$_2$ and Re(CO)$_3$-(PPh$_3$)(Br)(=COCH$_2$CH$_2$NH) (III) with NaH were unsuccessful. However, I is deprotonated by n-BuLi, PhLi or NaNp and III is deprotonated by n-BuLi to produce the imine complexes, Re(CO)$_4$(Br)(C=NCH$_2$CH$_2$O)$^-$ Li$^+$ and Re(CO)$_3$-(PPh$_3$)(Br)(C=NCH$_2$CH$_2$O)$^-$ Li$^+$ (eq. 5). These anionic imine compounds have IR spectra with ν(CO) relative intensities similar to their aminooxycarbene

$$Re(CO)_3(L)(Br)(=\overline{COCH_2CH_2NH}) \xrightarrow[-n\text{-BuH}]{n\text{-BuLi}}$$

$$Re(CO)_3(L)(Br)(\overline{C=NCH_2CH_2O})^- \xrightarrow{Me_3O^+}$$

fac-Re(CO)$_3$(L)(Br)[=$\overline{COCH_2CH_2N}$(CH$_3$)]

(IV: L = PPh$_3$;

V: L = CO)

(5)
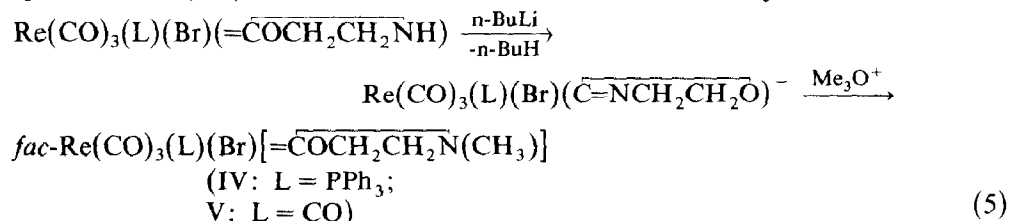
precursors (I and III), but the ν(CO) positions are about 15–20 cm^{-1} lower.

Table 3

^{13}C NMR data for the complexes in $CDCl_3$ solvent at room temperature [a]

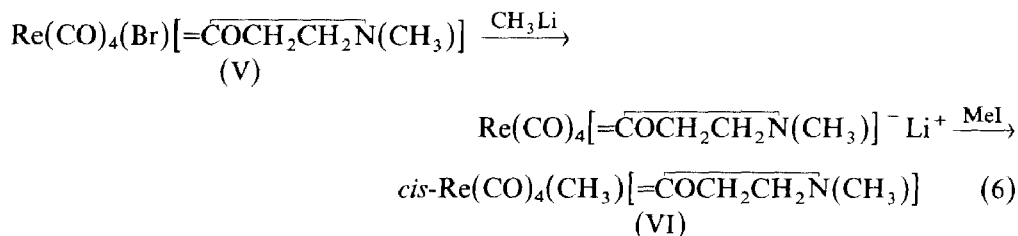| Complex	Carbene C	Carbonyl	OCH_2	NCH_2	Others
I [b]	208.19	188.60 186.09 185.13	73.24	45.59	
II [c]	217.18	193.12 192.72 188.81	71.94	44.36	
III [c]	216.88(d) [e]	194.59 (d) [f] 189.19 (d) [g] 189.31 (d) [h]	71.46	43.48	133.36 (d) 132.72, 132.13 129.82 127.74 (d) (PPh$_3$)
IV [d]	213.02 (d) [i]	194.65 (d) [j] 191.80 (d) [k] 191.13 (d) [l]	70.74	52.33	37.94 (NCH$_3$); 134.81 (d) 134.46, 134.26, 130.85 128.82 (d) (PPh$_3$)
V	208.56	185.51 184.82 [m] 183.24	70.30	51.32	37.49 (NCH$_3$)
VI	213.15	191.18 [m] 190.19 187.98	69.95	50.66	37.02 (NCH$_3$) − 32.73 (ReCH$_3$)
VII [d]	219.40 218.90	196.52 196.26 194.45 191.84	72.05 71.51	54.86 45.14	146.90, 146.02, 144.93, 142.39, 141.67 (C(3) of pz); 137.93, 136.12, 134.66, 132.03 (C(5) of pz); 107.64, 106.70, 106.51, 105.43, 105.33, 104.88 (C(4) of pz)
VIII [d]	209.69	not observed	70.63	45.59	146.39, 144.74 (C(3) of pz); 135.42 (C(5) of pz); 106.57, 106.36 (C(4) of pz)

[a] Chemical shifts in δ (relative to Si(CH$_3$)$_4$) and coupling constants in Hz. [b] In CD$_3$CN solvent. [c] In CD$_2$Cl$_2$ solvent. [d] In acetone-d_6 solvent. [e] J(PC) 8.76 Hz. [f] J(PC) 8.60 Hz, CO cis to PPh$_3$. [g] J(PC) 60.1 Hz, CO trans to PPh$_3$. [h] J(PC) 7.39 Hz, CO cis to PPh$_3$. [i] J(PC) 9.90 Hz, cis to PPh$_3$. [j] J(PC) 6.75 Hz, CO cis to PPh$_3$. [k] J(PC) 235 Hz, CO trans to PPh$_3$. [l] J(PC) 7.40 Hz, CO cis to PPh$_3$. [m] Two CO groups trans to each other.

The N atom of the anionic imine complexes reacts with Me$_3$O$^+$ BF$_4^-$ to give the *N*-methyl carbenes, Re(CO)$_4$(Br)($=\overline{COCH_2CH_2NMe}$) (V) and Re(CO)$_3$-(PPh$_3$)(Br)-($=\overline{COCH_2CH_2NMe}$) (IV) (eq. 5) in 64 and 78% isolated yields. The CH$_2$CH$_2$ region of the ^{1}H NMR spectrum of Re(CO)$_3$(PPh$_3$)(Br)($=\overline{COCH_2CH_2NMe}$) (IV) shows a pattern similar to that in III (4 sets of multiplets at 3.18, 3.34, 3.52 and 4.18 ppm) as expected for an ABCD system. The 3 ν(CO) bands of IV and 4 ν(CO) bands of V in their IR spectra (Table 1) suggest that they have *facial* and *cis* structures, respectively, as for the related complexes I and III. The ^{13}C NMR spectrum of V has 3

carbonyl peaks, 185.51, 184.82 and 183.24 ppm, with approximate relative intensities of 1/2/1.

The reaction of $Re(CO)_4(Br)(=\overline{COCH_2CH_2N}H)$ with n-BuLi gives not only the deprotonated anionic imine compound $Re(CO)_4(Br)(\overline{C=NCH_2CH_2O})^-$ Li^+, but apparently also the reduced $Re(CO)_4(=\overline{COCH_2CH_2N}H)^-$ Li^+ product, as suggested by the generation of a small amount (10%) of a byproduct, $Re(CO)_4(CH_3)(=\overline{COCH_2CH_2N}H)$ which was identified by its IR and ^1H NMR spectra ($\nu(CO)$, in CH_2Cl_2: 2068m, 1954vs, 1919s cm^{-1}; δ, in $CDCl_3$: 0.06 (s, 3H, ReMe); 3.70 (t, 2H, J 9.2 Hz, NCH_2); 4.58 (t, 2H, J 9.5 Hz, OCH_2) 7.44 (br, 1H, NH) ppm).

The reaction of $Re(CO)_4(Br)(=\overline{COCH_2CH_2N}Me)$ (V) and methyl lithium in THF at $-78°C$ generates $Re(CO)_4(=\overline{COCH_2CH_2N}Me)^-$ Li^+ whose IR spectrum ($\nu(CO)$: 2002s, 1910s, 1872vs cm^{-1}) is similar to that reported previously for $Mn(CO)_4(PPh_3)^-$ Na^+ [14] at 1941s, 1846ms, 1815vs cm^{-1}. This anionic intermediate reacts with MeI to give $Re(CO)_4(CH_3)(=\overline{COCH_2CH_2N}Me)$ (VI) in 64% yield (eq. 6). The presence of 4 $\nu(CO)$ bands in the IR spectrum (Table 1) of VI indicates that it has a *cis* structure.

$$Re(CO)_4(Br)[=\overline{COCH_2CH_2}N(CH_3)] \xrightarrow{CH_3Li}$$
$$(V)$$

$$Re(CO)_4[=\overline{COCH_2CH_2}N(CH_3)]^- Li^+ \xrightarrow{MeI}$$

$$cis\text{-}Re(CO)_4(CH_3)[=\overline{COCH_2CH_2}N(CH_3)] \qquad (6)$$
$$(VI)$$

Recently there has been considerable theoretical [15] and synthetic [16] interest in carbene-alkyl complexes as models for possible species present on catalyst surfaces in the Fischer–Tropsch reaction. There are, however, only two known examples of carbene-alkyl complexes also containing CO ligands, $Ir(Cl)(CO)(PPhMe_2)_2(Me)$-$(=C(OMe)Me)^+$ PF_6^- [17] and the dinuclear $Me(CO)_3Re(\mu\text{-}PPh_2)_2W(CO)_3$-$(=C(OEt)Me)$ [18]. Thus, we were interested in exploring the possibility of CH_3 migration onto the carbene or CO ligand in complex VI. Unfortunately, refluxing PPh_3 or PMe_3 with VI in benzene generates very low yields of only phosphine-substituted products, possibly $fac\text{-}Re(CO)_3(PR_3)(CH_3)(=\overline{COCH_2CH_2N}Me)$, although efforts to characterize it were unsuccessful. Also photolysis of PPh_3 of PMe_3 with VI in THF gives primarily decomposition products. The lack of CH_3 migration in this
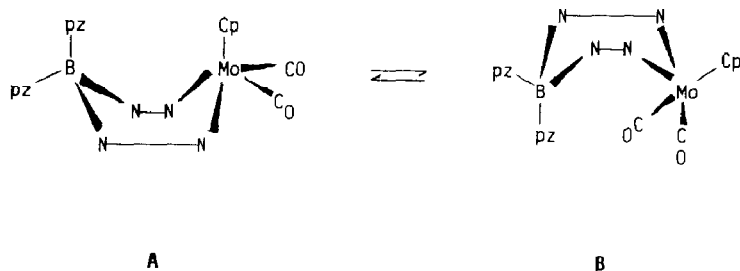

A   B

Fig. 1. Possible isomers of $[\eta^2\text{-}B(pz)_4](\eta^5\text{-}C_5H_5)(CO)_2Mo$.

system may reflect the unreactivity of $MeRe(CO)_5$ which does not give the acyl complex $MeCORe(CO)_5$ even under 320 atm of CO at $140 °C$; further heating to $200 °C$ leads only to $Re_2(CO)_{10}$ [19a]. There also appear to be no reports of CH_3 migration in reactions of $MeRe(CO)_5$ with phosphines [19b,c].

The reaction of $Re(CO)_4(Br)(=\overline{COCH_2CH_2N}H)$ (I) with $Na(C_5H_5)$ in refluxing THF gives only the deprotonated product $Re(CO)_4(Br)(\overline{C=NCH_2CH_2O})^-$ Na^+, as determined by the IR spectrum of the solution. When I reacts with Li^+ $(C_5Me_5)^-$, no stable complex could be isolated. However, complex I reacts with the hydrotris(pyrazolyl)borate ligand, $HB(pz)_3^-$, in refluxing THF for 18 h to yield $[\eta^2\text{-}HB(pz)_3]Re(CO)_3(=\overline{COCH_2CH_2N}H)$ (VII) (eq. 7). The IR spectrum of VII

$$K[HB(pz)_3] + Re(CO)_4(Br)(=\overline{COCH_2CH_2N}H) \xrightarrow{THF}$$
$$(I)$$

$$[\eta^2\text{-}HB(pz)_3]Re(CO)_3(=\overline{COCH_2CH_2N}H) + KBr + CO \qquad (7)$$
$$(VII)$$
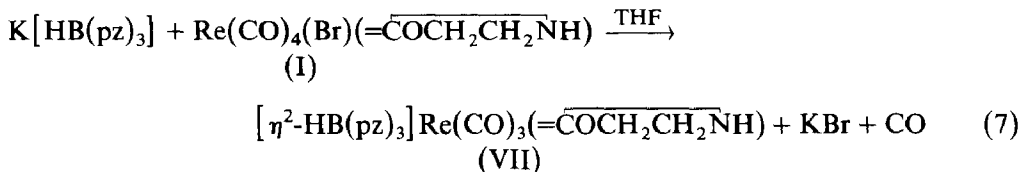
exhibits three strong bands of approximately equal intensity at 2033, 1930 and 1894 cm^{-1}, which is consistent with a *facial* arrangement of the three CO ligands. In order to accommodate the 18 electron rule, the presence of three carbonyls and one carbene ligand requires that only two of the three pyrazolyl groups in $HB(pz)_3^-$ coordinate to the metal which leaves the third one uncoordinated. Although the IR spectrum in the ν(CO) region of VII is consistent with the presence of only one *fac* isomer, the four CO and two carbene-C resonances in the ^{13}C NMR spectrum suggest the presence of two isomers. The structures of these isomers are not entirely clear. Previously, two isomers were observed [20] in NMR spectra of $[\eta^2\text{-}B(pz)_4](\eta^5\text{-}Cp)(CO)_2Mo$ and attributed to the two structures in Fig. 1, resulting from the shallow boat configuration of the chelate ring. Similar structures were proposed [21] for the two observed isomers of $CpRu[\eta^2\text{-}HB(3,5\text{-}Me_2pz)_3](CO)$. It is possible that VII exists as similar isomers; however, the two isomers resulting from interchanging the non-coordinated H and pz groups on the B cannot be excluded. The ^1H NMR spectrum of VII at room temperature consists of multiplets at 3.68 and 4.57 ppm and a broad band at 9.26 ppm which can be assigned to the NCH_2CH_2O and NH protons of the aminooxycarbene group and a complex group of resonances between 6.0 and 8.0 ppm which are due to the protons on the pyrazolyl rings. The two multiplets for the OCH_2 and NCH_2 protons suggest that more than one isomer is present. The complicated pattern for H(3), H(4) and H(5) in the pyrazolyl ligand also suggests the presence of isomers.

Refluxing the bidentate derivative $[\eta^2\text{-}HB(pz)_3]Re(CO)_3(=\overline{COCH_2CH_2N}H)$ in THF (2 days, no reaction) or dimethylformamide (1 day, decomposition) does not force the third pyrazolyl group to coordinate to the metal; however, when a THF solution of $[\eta^2\text{-}HB(pz)_3]Re(CO)_3(=\overline{COCH_2CH_2N}H)$ is photolyzed with UV light, the tridentate $[\eta^3\text{-}HB(pz)_3]Re(CO)_2(=\overline{COCH_2CH_2N}H)$ (VIII) is obtained (eq. 8).

$$[\eta^2\text{-}HB(pz)_3]Re(CO)_3(=\overline{COCH_2CH_2N}H) \xrightarrow{h\nu}{THF}$$
$$(VII)$$

$$[\eta^3\text{-}HB(pz)_3]Re(CO)_2(=\overline{COCH_2CH_2N}H) + CO \qquad (8)$$
$$(VIII)$$
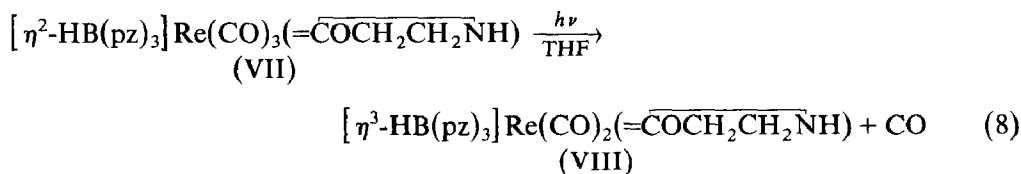
The IR and ^{1}H NMR spectra of VIII are consistent with the presence of a tridentate pyrazolylborate ligand. The presence of 2 ν(CO) bands of approximately equal intensity at 1923 and 1829 cm^{-1} indicates that the two CO ligands are *cis* to each other [22]. The ^{1}H NMR spectrum (Table 2) exhibits two sets of pyrazolyl resonances with an intensity ratio of 2/1. Assignments of the H(3), H(4) and H(5) protons were made following those of Trofimenko [21] and are given in Table 2. Attempts to convert VIII back to VII by reacting THF solutions of VIII with up to 35 atm of CO at 75°C yielded no evidence for the reformation of VII (the only metal carbonyl compound is starting material VIII).

Conclusion

The carbene ligand in *cis*-Re(CO)$_4$(Br)($=\overline{\text{COCH}_2\text{CH}_2\text{NH}}$) (I) is sufficiently stable that a variety of reactions can be performed on I without affecting the carbene ligand. The NH group maybe deprotonated and the resulting imine methylated (eq. 5). The CO ligands may be substituted by PPh$_3$ (eq. 3) or HB(pz)$_3^-$ (eq. 7 and 8), and the Br ligand may be replaced in the *N*-methyl complex V by a methyl.

Acknowledgment

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