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Synthesis, Substitution, and Isomerization Reactions of *trans*-Re(CO)$_4$LX (L = Group 15 Donor Ligands; X = Br, I)

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The cleavage of $Re_2(CO)_8L_2$ with X_2 (X = I, L = PPh_3, $P(OMe)Ph_2$, $P(OMe)_3$, $P(OMe)_2Ph$, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, $P(O\text{-}o\text{-}tol)_3$, $P(O^iPr)_3$, $P(CH_2C_6H_5)_3$; X = Br, L = PPh_3, $P(OMe)_3$, $P(OMe)_2Ph$, PMe_2Ph, $P(OPh)_3$, $P(CH_2C_6H_5)_3$) in CH_2Cl_2 gives *trans*-Re(CO)$_4$LX in yields between 20% and 50% as well as *cis*-Re(CO)$_4$LX (>50%). Reactions of $Re_2(CO)_9L$ with Br_2, by contrast, gave only *cis*-Re(CO)$_4$LBr and $Re(CO)_5Br$, while reactions of $Re_2(CO)_9PBz_3$ (Bz = $CH_2C_6H_5$) with I_2 gave $Re(CO)_5I$ as well as a mixture of *cis*- and *trans*-Re(CO)$_4$PBz$_3$I (ratio 72:28). The PBz_3-containing product ratio could be modified by addition of I^- (35:65 isomer ratio) and Br^- (15:85, cis-trans ratio; product contained mixture of $Re(CO)_4PBz_3I$ and $Re(CO)_4PBz_3Br$). The data for the cleavage reactions of $Re_2(CO)_{10-n}L_n$ (n = 1, 2) can be explained by an electrophilic attack of halogen, followed by two competing pathways (concerted, associative) involving attack of the nucleophile. It is predicted that in the *total* product spectrum ($Re(CO)_5X$, $Re(CO)_4LX$) that a maximum of 50% *trans*-Re(CO)$_4$LX can be obtained by the halogen cleavage route. An IR kinetic investigation of the *trans*- to *cis*-Re(CO)$_4$LX isomerization reaction is consistent with an intramolecular rearrangement process that is influenced by the halide (I < Br) and the ligand ($P(O\text{-}o\text{-}tol)_3 < P(Bz)_3 \sim P(OPh)_3 \sim PMe_2Ph < PMePh_2 \sim PPh_3 < P(O^iPr)_3 < P(OMe)_3$). Reaction of *trans*-Re(CO)$_4$PBz$_3$I with L (L = $P(OPh)_3$, *t*-BuNC) at 100 °C in C_6D_6 revealed that isomerization (60%) was more rapid than substitution (<8%). However, reaction with Me_3NO/CH_3CN or PdO/*t*-BuNC gave product ratios of *cis*- and *trans*-Re(CO)$_3$(PBz$_3$)LI (L = CH_3CN, *t*-BuNC) that were consistent with substitution preceding isomerization. The Re–CO bonds in *trans*-Re(CO)$_4$PBz$_3$I are less prone to cleavage than equivalent cis Re–CO bonds in cis-Re(CO)$_4$PBz$_3$I.

Introduction

There are numerous physical methods that have been used to establish the identity of the $M_2(CO)_{10-x}L_x$ (M = Mn, Re; x = 1, 2) isomers formed in the reaction between $M_2(CO)_{10}$ and L. These techniques include IR[1-3] and NMR[4] spectroscopy, mass spectrometry,[3] and X-ray crystallography.[5] Alternatively, chemical reactions, which include metal–metal bond cleavage reactions, can in principle also be used to access the dimer isomer composition.[2,6] Surprisingly very few investigations have been reported on the use of the halogen cleavage reaction to identify the isomers of $M_2(CO)_{10-x}L_x$ (L = group-15 donor ligands; x = 1, 2). Indeed there are reports on the synthesis of both cis and trans isomers of M(CO)$_4$LX (M = Mn,[2,7] Re;[8-10] L = phosphine, phosphite; X = halogen) on cleavage of $M_2(CO)_{10-x}L_x$ complexes, but correlation of dimer isomers with the cleaved monometallic fragment isomers has not been explored in detail. Further, *trans*-M(CO)$_4$LX (M = Mn, Re) is reported to readily isomerize to the cis isomer.[10] Indeed the trans isomer cannot be prepared by conventional substitution reactions of M(CO)$_5$X.[11] Although numerous kinetic studies have been reported on the cis–trans isomerization reaction of octahedral M(CO)$_4$L$_2$ (M = Cr, Mo, W) and other related octahedral complexes,[12] no report has appeared on the related trans–cis isomerization reactions of Re(CO)$_4$LX. We thus report a preliminary investigation of the kinetics of the isomerization of the Re complexes and a comparison of the results with the kinetic data available on other cis–trans isomerization reactions of octahedral M(CO)$_4$L$_2$ complexes.[12]

Finally, the chemistry of *trans*-Re(CO)$_4$LX has to date not been investigated. It is well-known that mutually trans CO groups are more labile to substitution than CO groups trans to either halides or group-15 donor ligands.[13] This would suggest that the CO groups in *trans*-Re(CO)$_4$LX could be more prone to substitution than the CO groups

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Table I. Analytical Data for the Complexes $Re(CO)_4(PR_3)X$

complex	mp/°C	anal.[a]/% C	anal.[a]/% H
trans-$Re(CO)_4(PPh_3)I$	142–143	39.34 (38.44)	2.35 (2.20)
trans-$Re(CO)_4P(O$-o-tol$)_3I$	111–113	38.26 (38.62)	2.57 (2.72)
trans-$Re(CO)_4(PMe_2Ph)I$	139–141	25.64 (25.59)	1.86 (1.97)
trans-$Re(CO)_4P(OPh)_3I$	127–128	35.81 (35.93)	1.95 (2.06)
cis-$Re(CO)_4(PBz_3)I$	119–120	41.53 (41.16)	2.86 (2.90)
trans-$Re(CO)_4(PBz_3)I$	148–149	42.05 (41.16)	2.90 (2.90)
cis-$Re(CO)_4(PBz_3)Br$	117–119	43.81 (43.99)	3.01 (3.10)
trans-$Re(CO)_4(PBz_3)Br$	134–135	43.74 (43.99)	3.01 (3.10)

[a] Calculated values in parentheses.

Table II. Recrystallization Solvents and Product Yields for the $Re(CO)_4(PR_3)I$ Complexes

PR_3	solvent system[a]	yields/% trans[a]	yields/% cis[b]
PPh_3	hexane	25	50
$P(O^iPr)_3$	hexane	15	35
$PMePh_2$	CH_2Cl_2	20	25
PBz_3	mesitylene	30	45
$P(O$-*o*-tol$)_3$	ethyl acetate/hexane	25	40
PMe_2Ph	CH_2Cl_2	30	40
$P(OPh)_3$	hexane	15	35

[a] *trans*-$Re(CO)_4LI$ isolated by recrystallization. [b] *cis*-$Re(CO)_4LI$ isolated by column chromatography on the mother liquor residues.

Table III. Infrared Data for the Complexes *trans*-$Re(CO)_4LI$[a]

L	ν(CO)/cm^{-1}	L	ν(CO)/cm^{-1}
PPh_3	2058 w, 1986 vs	$PMePh_2$	2056 w, 1984 vs
$P(OMe)Ph_2$	2052 w, 1998 vs	PBz_3	2056 w, 1984 vs
$P(OMe)_3$	2046 w, 1995 vs	$P(O$-*o*-tol$)_3$	2058 w, 2010 vs
$P(O^iPr)_3$	2046 w, 1995 vs	PMe_2Ph	2058 w, 1981 vs
$P(OMe)_2Ph$	2056 w, 2000 vs	$P(OPh)_3$	2056 w, 2014 vs

[a] Recorded in CH_2Cl_2.

Table IV. ^1H and ^{31}P NMR Data for the Complexes *trans*-$Re(CO)_4LI$[a]

L	^1H (δ)/ppm CH_3 or CH_2[b]	^1H (δ)/ppm aromatic[c]	^{31}P (δ)/ppm	^{31}P (δ)/ppm[d]
PPh_3		6.90–6.96, 7.15–7.23	13.3	−4.9
$P(OMe)Ph_2$	2.68 (13)		104.5	93.5
$P(OMe)_3$	2.86 (12)		111.1	100.7
$P(O^iPr)_3$	0.95 (6), 4.13 m		101.0	90.9
$P(OMe)_2Ph$	2.82 (13)	6.38–6.99, 7.46–7.57	128.1	122.2
$PMePh_2$	1.54 (9)	6.91–7.06, 7.24–7.35	−10.0	−25.2
PBz_3	2.92 (9)		5.1	−18.6
$P(O$-*o*-tol$)_3$	2.09	6.73–6.82, 7.24–7.29	101.4	88.3
PMe_2Ph	1.97 (7)	6.91–7.11, 7.23–7.31	−10.2	−24.9
$P(OPh)_3$		6.49–7.06, 7.19–7.31	105.2	91.8

[a] Recorded in C_6D_6 relative to internal TMS (^1H) or external H_3PO_4(^{31}P) standards. [b] Doublet coupling constant, *J*(PH) (Hz), in parenthesis. [c] Multiplet range quoted. [d] Data for *cis*-$Re(CO)_4LI$.

Table V. *cis/trans*-$Re(CO)_4LX$ Product Composition Obtained from the Reaction of $Re_2(CO)_8L_2$ with X_2

X_2	L	products $Re(CO)_4LBr$ cis	products $Re(CO)_4LBr$ trans	products $Re(CO)_4LI$ cis	products $Re(CO)_4LI$ trans
Br_2	$P(OMe)_2Ph$	53	47		
Br_2	PMe_2Ph	69	31		
Br_2	PPh_3	54	46		
Br_2	$P(OPh)_3$	53	47		
Br_2	$P(OMe)_3$	59	41		
Br_2	PBz_3[a]	60	40		
I_2	PBz_3			57	43
I_2	PBz_3[b]			62	38
I_2	PBz_3[c]	14	14	57	14
I_2	PPh_3			68	32
I_2	$P(OMe)Ph_2$			71	29
I_2	$P(OMe)_3$			68	32
I_2	$P(O^iPr)_3$			61	39
I_2	$P(OMe)_2Ph$			72	28
I_2	$PMePh_2$			70	30
I_2	$P(O$-*o*-tol$)_3$			65	35
I_2	PMe_2Ph			69	31
I_2	$P(OPh)_3$			68	32

[a] Estimated from IR data. [b] Performed in the presence of I^- (10-fold excess). [c] Performed in the presence of Br^- (10-fold excess).

in *cis*-$Re(CO)_4LX$. Herein we report our findings on the reactivity of the CO ligands in *trans*-$Re(CO)_4LX$.

Experimental Section

General Methods. $Re_2(CO)_{10}$ was obtained from Strem Chemicals. Phosphine ligands were obtained from various sources (Strem, Aldrich, Merck). I_2 and Br_2 were purchased from BDH and Merck, respectively. $Me_3NO{\cdot}2H_2O$ was purchased from Aldrich and dried by azeotrope in toluene prior to use. *diax*-$Re_2(CO)_8(PR_3)_2$ and *cis*-$Re(CO)_4(PR_3)X$ (PR_3 = PPh_3, $P(OMe)Ph_2$, $P(OMe)_3$, $P(OMe)_2Ph$, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, $P(O$-*o*-tol$)_3$, $P(O^iPr)_3$, $P(Bz)_3$; Bz = $CH_2C_6H_5$) complexes were prepared by known routes.[14,15] Reactions were routinely carried out under nitrogen in degassed solvents distilled from appropriate drying agents prior to use. Infrared spectra were recorded on a Brucker IFS 85 and NMR (^1H, ^{31}P) spectra on a Brucker AC 200 NMR spectrometer. Melting points were recorded on a Köffler hot stage apparatus and are uncorrected. Microanalyses were performed by the Division of Energy Technology, CSIR, Pretoria, RSA.

Synthesis of *trans*-$Re(CO)_4LX$ from Reaction of $Re_2(CO)_8L_2$ with X_2 (X = I, L = PPh_3, $P(OMe)Ph_2$, $P(OMe)_3$, $P(OMe)_2Ph$, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, $P(O$-*o*-tol$)_3$, $P(O^iPr)_3$, $P(CH_2C_6H_5)_3$; X = Br, L = PPh_3, $P(OMe)_3$, $P(OMe)_2Ph$, PMe_2Ph, $P(OPh)_3$, $P(CH_2C_6H_5)_3$). (a) Preparative Scale Reaction. Slow addition of a solution of X_2 (X = Br, I) (0.9 equiv) in CH_2Cl_2 (5 mL) to *diax*-$Re_2(CO)_8L_2$ (0.2 mmol) in CH_2Cl_2 (20 mL) gave a mixture of *cis*- and *trans*-$Re(CO)_4(L)X$ as detected by IR spectroscopy. After 30 min an aqueous $Na_2S_2O_3$ solution was added to the CH_2Cl_2 solution to neutralise excess X_2. The CH_2Cl_2 fraction was then separated from the aqueous layer, dried over anhydrous $MgSO_4$, and filtered through Celite. The solvent was then removed under reduced pressure. The required trans products (X = I) were isolated by fractional crystallization from mesitylene, hexane, CH_2Cl_2/hexane, or ethyl acetate/hexane and the cis products were obtained by column chromatography (silica gel; benzene/hexane is eluant) (see Table I for analytical data,

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Table VI. Products Obtained from the Reaction of $Re_2(CO)_9L$ with X_2

		product ratios			
		$Re(CO)_4LBr$		$Re(CO)_4LI$	
X_2	L	cis	trans	cis	trans
Br	$P(O\text{-}o\text{-}tol)_3$	100	0		
Br	$P(OMe)_3$	100	0		
Br	PPh_3	100	0		
Br	$PMePh_2$	100	0		
Br	PBz_3	100	0		
I	PBz_3			72	28
I[a]	PBz_3			35	65
I[b]	PBz_3	5	60	15	20

[a] Performed in the presence of I^- (10-fold excess). [b] Performed in the presence of Br^- (10-fold excess).

Table II for crystallization conditions and yields, and Tables III and IV for spectroscopic data).

(b) NMR Scale Reaction. Similar reactions (X = I) were performed in C_6D_6 in an NMR tube and the results of the preparative scale reactions confirmed by ^1H NMR and ^{31}P NMR spectroscopy (Table V). The NMR samples were then heated at 75 °C for 30 min and the *relative* isomerization rates determined from the change in intensities with time of the product and reactant absorptions in the ^1H and ^{31}P NMR spectra.

Reaction of $Re_2(CO)_9L$ with X_2 (X = Br, L = PBz_3, $P(O\text{-}o\text{-}tol)_3$, $P(OMe)_3$, PPh_3, $PMePh_2$; X = I, L = PBz_3). Addition of a solution of X_2 (0.9 equiv) in C_6D_6 (0.05 mL) to a solution of $Re_2(CO)_9L$ (0.1 mmol) in C_6D_6 (0.4 mL) in an NMR tube at room temperature resulted in a rapid, almost complete, disappearance of the starting material to yield one new complex, *cis*-$Re(CO)_4LX$, as identified by comparison with the independently synthesized complexes. Similar reactions were performed for L = PBz_3 with 0.5 and 1.1 equiv of X_2 (see text) and the products identified by NMR (^1H, ^{31}P) spectroscopy.

Reaction of $Re_2(CO)_{10-n}(PBz_3)_n$ (n = 1, 2) with I_2 in the Presence of $[NEt_4]X$ (X = I, Br). Addition of a solution of I_2 (1.1 equiv) in CH_2Cl_2 (2 mL) to a solution of $Re_2(CO)_{10-n}(PBz_3)_n$ (0.05 mmol) (n = 1, 2) and $[NEt_4]X$ in CH_2Cl_2 (2 mL)/MeOH (5 mL) resulted in complete reaction of the starting material as detected by IR spectroscopy. After solvent removal under vacuum, the residue was redissolved in CH_2Cl_2 (2 mL), filtered through cotton wool, and pumped to dryness under vacuum. The product was finally dissolved in C_6D_6 and transferred to a NMR tube, and the ^1H and ^{31}P NMR spectra were recorded on the crude reaction mixture. Product ratios are given in Tables V and VI.

Reaction of $Re(CO)_4(PBz_3)I$ with Me_3NO in CH_3CN. (a) To a solution of *cis*-$Re(CO)_4(PBz_3)I$ (0.01 mmol) in CH_3CN (2 mL) was added Me_3NO (1.0 equiv) as a solid. The solution was stirred for 30 min and the solvent removed under vacuum. The residue was extracted with C_6D_6 (0.4 mL), filtered through cotton wool, and transferred to an NMR tube and the ^1H and ^{31}P NMR spectra were recorded (see Tables VII and VIII).

(b) A similar reaction to that described above in (a) was performed by using *trans*-$Re(CO)_4(PBz_3)I$. The ^{31}P NMR spectrum recorded on the reaction mixture revealed three resonances (see Tables VII and VIII). After heating the sample to 80 °C for 45 min only the most intense resonance remained. Addition of *t*-BuNC (1.1 equiv) to the NMR tube, followed by heating at 80 °C for 10 min, resulted in clean conversion to only one new resonance in the ^{31}P spectrum. This corresponded to *fac*-$Re(CO)_3(CNBu\text{-}t)(PBz_3)I$ as determined by correlation with the spectrum of an independently synthesized complex.

(c) An equimolar mixture of *cis*-$Re(CO)_4(PBz_3)I$ and $Re(CO)_5I$ (0.01 mmol) was reacted as described above in (a). The ^{31}P NMR spectra of the product mixture showed no evidence for the formation of any new ^{31}P-containing products, whereas the ^1H NMR spectrum revealed two new resonances corresponding to **19** and **20** (L = CH_3CN) (see Table VIII). Addition of *t*-BuNC to this reaction mixture followed by heating at 80 °C for 10 min resulted in the clean conversion of the two resonances to two new NMR signals in the ^1H spectrum. These new resonances corresponded to $Re(CO)_{5-x}(CNBu\text{-}t)_xI$ (x = 1, 0.72 ppm, 63%; x = 2, 0.87 ppm, 25%).[16] Heating of this reactant solution (80 °C, 45 min) resulted in the formation of *fac*-$Re(CO)_3(CNBu\text{-}t)(PBz_3)I$ (5% of P-containing products) as detected in the ^{31}P NMR spectrum.

Table VII. ^1H and ^{31}P NMR Data for the Complexes $Re(CO)_{4-x}L_x(PBz_3)I$[a,b] (x = 1, 2)

	^1H (δ)/ppm		
	L (CH_3)	Bz (CH_2)[c]	^{31}P (δ)/ppm
x = 1, L = CH_3CN			
15a	0.24	3.12 (7, 15, 9)[d]	−22.1
16a	0.43	3.32 (7)	−19.5
17a	0.58	2.92 (9)	2.0
x = 1, L = *t*-BuNC			
15b	0.77	3.58 (8, 15, 45)[d]	−22.5
16b	0.84	3.59 (8)	−16.8
17b	0.97	3.18 (9)	2.9
x = 2, L = *t*-BuNC			
21b	0.93 1.02	3.80 (8)	−13.3

[a] Recorded in C_6D_6 relative to internal TMS or external H_3PO_4 standards. [b] J(PH) coupling constants in parentheses. [c] Aromatic proton resonances not resolved and not quoted. [d] $J(PH_1)$, $J(H_aH_b)$, $J(PH_b)$.

Table VIII. Product Distribution for the Reaction of $Re(CO)_4(PBz_3)I$ with L (L = CH_3CN (a), *t*-BuNC (b))

	product distribution/%					
reactants	15	16	17	19	20	21
Me_3NO/CH_3CN						
cis-$Re(CO)_4(PBz_3)I$	33	66				
trans-$Re(CO)_4(PBz_3)I$	89	7	4			
cis-$Re(CO)_4(PBz_3)I/Re(CO)_5I$[a]				85	15	
trans-$Re(CO)_4(PBz_3)I/Re(CO)_5I$[a]				75	25	
PdO/*t*-BuNC						
cis-$Re(CO)_4(PBz_3)I$	86	12			2	
trans-$Re(CO)_4(PBz_3)I$	40	24	5		3	28
cis/*trans*-$Re(CO)_4(PBz_3)I$[a]	62	9			2	17
trans-$Re(CO)_4(PBz_3)I/Re(CO)_5I$[a]				89	11	

[a] 1:1 ratio.

(d) A similar reaction to that described above in (c) was performed by using *trans*-$Re(CO)_4(PBz_3)I$ and similar results were obtained. Trans–cis isomerization of $Re(CO)_4(PBz_3)I$ as well as ligand exchange was also detected by ^{31}P NMR spectroscopy after heating the mixture at 80 °C.

Reaction of $Re(CO)_4(PBz_3)I$ with *t*-BuNC/PdO. (a) A solution of *cis*-$Re(CO)_4(PBz_3)I$ (0.01 mmol) and *t*-BuNC (1 equiv) in C_6D_6 (0.4 mL) was heated at 50 °C for 15 min in an NMR tube in the presence of a catalyst (PdO, 0.2 equiv). No change was observed in the ^1H and ^{31}P NMR spectra. After heating at 100 °C for 35 min two new resonances were observed in the ^{31}P NMR spectrum, which corresponded to *mer*- and *fac*-$Re(CO)_3(PBz_3)(CNBu\text{-}t)I$ as determined by comparison with independently synthesized and characterized complexes.

(b) A similar reaction to that described above in (a) was performed by using *trans*-$Re(CO)_4(PBz_3)I$. No reaction was detected after heating at 50 °C for 15 min. After heating at 100 °C for 35 min four new resonances were observed, in the ^{31}P NMR spectrum, corresponding to four new products as well as *cis*-$Re(CO)_4(PBz_3)I$ (10% of P-containing products; see Table VIII for a listing of the yields of products formed in the reaction).

(c) A similar reaction to those described above was performed by using an equimolar mixture of *cis*- or *trans*-$Re(CO)_4(PBz_3)I$ and $Re(CO)_5I$ (0.01 mmol). The only substituted products observed were $Re(CO)_{5-x}(CNBu\text{-}t)_xI$ (x = 1, 2)[16] as detected by ^1H NMR spectroscopy and *cis*-$Re(CO)_4(PBz_3)I$ as detected by ^1H and ^{31}P NMR spectroscopy.

Isomerization of *trans*-$Re(CO)_4(PBz_3)I$ in the Presence of L (L = $P(OPh)_3$, *t*-BuNC). *trans*-$Re(CO)_4(PBz_3)I$ (0.02 mmol) and L (5 equiv) were dissolved in toluene-d_8 (0.4 mL) in an NMR tube. The reactions were monitored by ^1H and ^{31}P NMR spectroscopy. The products observed after heating at 100 °C for

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[16] Coville, N. J.; Johnston, P.; Leins, A. E.; Markwell, A. J. *J. Organomet. Chem.* **1989**, *378*, 401.

Table IX. Rate Constants for the Trans–Cis Isomerization of $Re(CO)_4LI$ Complexes

L	$k \times 10^5/s^{-1}$				θ^b	pK_a^c
	70 °C	80 °C	90 °C	100 °C		
$P(O\text{-}o\text{-}tol)_3$		1.5	6.5	21	141	−1.83
PBz_3		5.1	13	28	165	
$P(OPh)_3$		5.5	11	53	128	−2
PMe_2Ph		6.5	13	61	122	6.5
$PMePh_2$		6.2	20	76	136	4.57
PPh_3	3.5	7.5	21		145	2.37
$P(O^iPr)_3$	13	17	45		130	4.08

[a] Qualitative data, derived from ^1H NMR spectroscopy, were also obtained for L = $P(OMe)_3$, $P(OMe)_2Ph$, and $P(OMe)Ph_2$ and indicated an increase in isomerisation $P(OMe)_3 > P(OMe)_2Ph > P(OMe)Ph_2 > P(O^iPr)_3$. [b] Tolman cone angle.[23] [c] pK_a values taken from Giering and co-workers.[24]

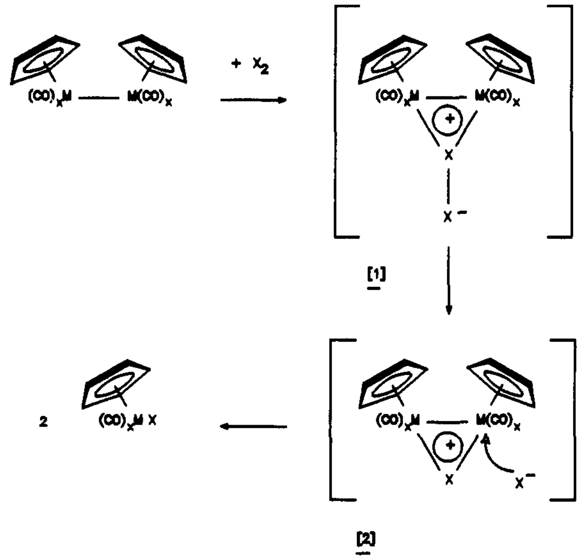
90 min were *cis*-$Re(CO)_4(PBz_3)I$ (60%), *fac*-$Re(CO)_3(PBz_3)LI$ (8%), and *cis*-$Re(CO)_4LI$ (8%), as well as starting material (24%).

Kinetic Investigation of the Isomerization of *trans*- to *cis*-$Re(CO)_4LI$ (L = PPh_3, $P(OMe)Ph_2$, $P(OMe)_3$, $P(OMe)_2Ph$, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, $P(O\text{-}o\text{-}tol)_3$, $P(O^iPr)_3$, $P(CH_2C_6H_5)_3$). Redistilled mesitylene was used as the reaction solvent in all the isomerization experiments. The reaction solutions were maintained at a constant temperature (±1 °C) in a sealed variable-temperature infrared cell (KIIC-VLTZ) preset at the required temperature. The reaction rates were followed spectroscopically. After sample introduction, the cell was sealed and the solution thermally equilibrated for 5 min prior to measurements. The reaction rates were monitored by measuring the increase in absorbance in the infrared spectrum of the characteristic ν(CO) band of *cis*-$Re(CO)_4(PR_3)I$ at ~2106 cm^{-1}. Spectra were recored at regular time intervals. The Quantitative Analysis software option of the infrared instrument was used to determine the absorbance area of the monitored peak. Measurements were usually made over 2 half-lives. Good linear plots of $\ln (A_\infty - A_t)$ vs t (A_∞ = absorbance at infinite time; A_t = absorbance at time t) were obtained. The rate constant (k) and half-lives ($t_{1/2}$) were determined from the slope of a plot of $\ln (A_\infty - A_t)$ versus t. Each reaction was performed at three different temperatures at constant concentrations of $Re(CO)_4(PR_3)I$. Rate and thermodynamic data are presented in Table IX.

Results and Discussion

Halogen Cleavage Reactions of *ax*-$Re_2(CO)_9L$. The cleavage of the dimers $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ by halogens has been studied in some detail and the reaction has been proposed to take place in a stepwise manner.[17,18] The first step is suggested to involve an electrophilic attack on the metal–metal bond by X_2 to yield a three-center transition state, 1 (Scheme I). This is followed by dissociation of the X–X bond and attack of 2 (Scheme I) by the X^- nucleophile. It is well-known that cleavage of $M_2(CO)_{10}$ (M = Mn, Re) by X_2 gives $M(CO)_5X$,[19] and a similar mechanism for this reaction may be anticipated. Indeed the kinetics of the cleavage reaction has been explored in some detail,[6e] especially by Poë and co-workers,[7,20,21] and their results are consistent with an electrophilic attack of halogen on the metal dimer.

Scheme I. Cleavage of $[(C_5H_5)M(CO)_x]_2$ with X_2 (M = Fe, x = 2; M = Mo, W, x = 3)



To further investigate the mechanism of this reaction we have studied the cleavage reactions of $Re_2(CO)_{10-x}L_x$ (x = 1, 2) with Br_2 and I_2 under varying conditions. Reaction of *ax*-$Re_2(CO)_9L$ (L = group-15 donor ligand) with Br_2 in C_6D_6 was monitored by IR and NMR spectroscopy and the results of our investigation are shown in Table VI. It can be seen that 100% *cis*-$Re(CO)_4LBr$ complex is formed in every reaction. The possibility of initial trans isomer formation followed by rapid rearrangement to the cis isomer can be ruled out (see below). Cleavage of $Re_2(CO)_9(PBz_3)$ with I_2 gave two PBz_3-containing complexes, *cis*-$Re(CO)_4(PBz_3)I$ (72%) and *trans*-$Re(CO)_4(PBz_3)I$ (28%). Cleavage of the dimer with I_2 in the presence of I^- ions ($[Et_4N]I$; 10-fold excess) again resulted in the formation of *cis*-$Re(CO)_4(PBz_3)I$ and *trans*-$Re(CO)_4(PBz_3)I$ but in a different product distribution (35%:65%) (see Table VI). To further explore the reaction, the effect of the addition of Br^- ions ($[NEt_4]Br$, 10-fold excess) to the reaction mixture containing *ax*-$Re_2(CO)_9(PBz_3)/I_2$ was investigated. This resulted, not unexpectedly, in the formation of four PBz_3-containing products, *cis*/*trans*-$Re(CO)_4PBz_3I$ and *cis*/*trans*-$Re(CO)_4PBz_3Br$. The cis/trans mixture (15/20) of the iodo isomers constituted 35% of the PBz_3 product. Of significance is the low yield of *cis*-$Re(CO)_4LBr$ (5%) and the high yield of *trans*-$Re(CO)_4(PBz_3)Br$ (60%) formed in the reaction. An explanation of the results is given below.

Since the rhenium dimer is asymmetrical, i.e., consists of two dissimilar monometallic fragments, $Re(CO)_4L$ and $Re(CO)_5$, electrophilic attack by a halogen, X_2, is proposed to lead to the unsymmetrical three-centered cationic intermediate (or transition state) 3 (Scheme II), with the charge associated with the more nucleophilic metal center, i.e., the $Re(CO)_4L$ entity. Consequently the nucleophilic attack will predominantly, if not exclusively, occur at the $Re(CO)_4L$ entity. Two pathways originating from 3 (Scheme II) are proposed; (i) a concerted intramolecular pathway via 4 in which the "nucleophile" is always associated with the dimer, resulting in the formation of *cis*-$Re(CO)_4LX$, and (ii) a dissociative pathway via 5 resulting in the formation of *cis*- and *trans*-$Re(CO)_4LX$. The following are factors in support of these two pathways:

(1) Cleavage of *ax*-$Re_2(CO)_9L$ with I_2 in the presence of Br^- results in formation of a mixture of *cis*- (15%) and *trans*-$Re(CO)_4LI$ (20%) and *cis*- (5%) and *trans*-$Re(CO)_4LBr$ (60%; 90% of Br-containing species). The high

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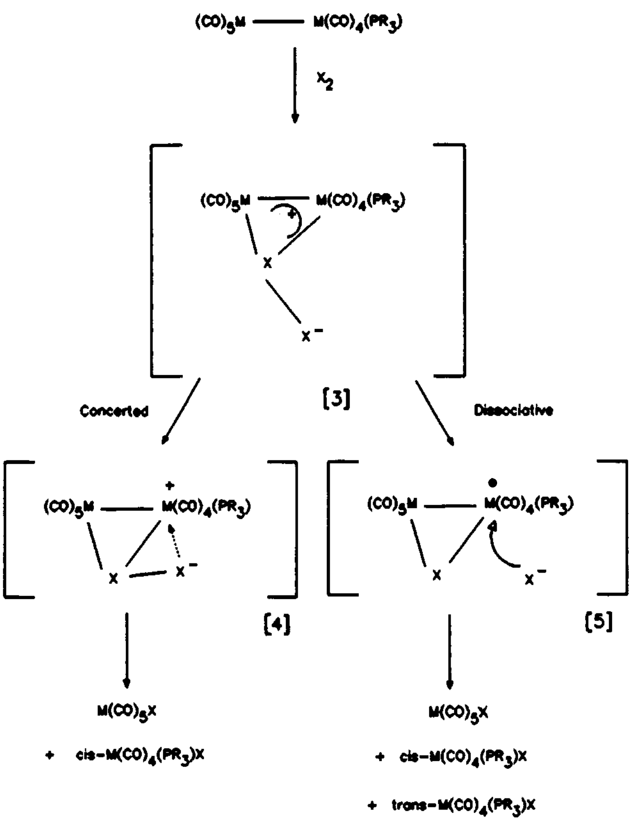
Scheme II. Cleavage of $Re_2(CO)_9(PR_3)$ with X_2



yield of *trans*-Re(CO)$_4$LBr provides convincing evidence that *external* attack of a nucleophile produced the trans isomer. This would suggest that the high yield of *trans*-Re(CO)$_4$LI also arises from this process, with the cis product resulting from the intramolecular attack from bound I_2. When the reaction is carried out in a nonpolar solvent, C_6D_6, the cis/trans ratio, as expected, increases (Table VI), since the intramolecular process will now be favored over the dissociative process.

(2) Cleavage of *ax*-$Re_2(CO)_9L$ with I_2 in the presence of I^- would be expected to increase the rate of reaction of the intermolecular pathway and result in an increase in the percentage of trans isomer formed. The appearance of *cis*-Re(CO)$_4$LI indicates that the concerted intramolecular pathway is not inhibited entirely by I^-. This result also provides confirmation that nucleophilic attack by X^- occurs at the substituted metal center (Re(CO)$_4$L) rather than at the unsubstituted metal center (Re(CO)$_5$). A change in the rate of the intermolecular pathway would not be expected to alter the product spectrum if nucleophilic attack on the three-center intermediate **3** (Scheme II) occurred at Re(CO)$_5$.

(3) Cleavage of *ax*-$Re_2(CO)_9L$ with X_2 results in exclusive formation of *cis*-Re(CO)$_4$LBr for X = Br, but in a mixture of *cis*- (72%) and *trans*-Re(CO)$_4$LI (28%) for X = I. These reactions were carried out in C_6D_6, a nonpolar solvent, and are consistent with the stabilization of the softer I^- in this solvent.

Halogen Cleavage Reaction of *diax*-$Re_2(CO)_8L_2$. Similar reactions as above were performed on the diaxially substituted derivatives. Since these complexes are symmetrical, addition of the halogens should result in a symmetrical three-center cationic intermediate (transition state) **6** (Scheme III).

Cleavage of *diax*-$Re_2(CO)_8L_2$ with X_2 resulted in the formation of both *cis*- and *trans*-Re(CO)$_4$LX (X = Br, ~60% and ~40%, respectively; X = I, ~70% and ~30%, respectively). Cleavage with I_2 in the presence of X^- (10-fold excess; [NEt$_4$]X) did not significantly alter the amount of *cis*-Re(CO)$_4$LX formed. The presence of excess I^- had a minimal effect on the amount of *trans*-Re(CO)$_4$LI formed, whereas excess Br^-, not unexpectedly, resulted in a decrease in the amount of *trans*-Re(CO)$_4$LI with a concomitant increase in the amount of *cis*- and *trans*-Re(CO)$_4$LBr products.

An analysis of these results suggests that the cleavage of *diax*-$Re_2(CO)_8L_2$ proceeds via a mechanism similar to that proposed for the cleavage of *ax*-$Re_2(CO)_9L$. The following are points of relevance:

(1) Since both sides of the dimer are substituted, cleavage reactions with halogens will give information on both the electrophilic and nucleophilic reactions.

(2) Models indicate that movement of the electrophile to either side of the dimer from **6** will lead to *cis*-Re(CO)$_4$LX. As discussed above the second step can give rise to either *cis*- and *trans*-Re(CO)$_4$LX. Hence a maximum of 50% trans product can be predicted for the reaction. Experimental results obtained for a wider range of L (see Table V) are consistent with this suggestion.

(3) Addition of I^- to the reaction does not significantly change the amount of *trans*-Re(CO)$_4$(PBz)$_3$I formed (40 ± 3%) in the reaction and is consistent with (2) above.

(4) Addition of Br^- to $Re_2(CO)_8(PBz_3)_2/I_2$ also did not significantly alter the amount of *cis*-Re(CO)$_4$(PBz$_3$)$_3$I formed in the reaction. Thus, it was only the route responsible for the generation of *trans*-Re(CO)$_4$(PBz$_3$)I that was modified by the external nucleophile. It is to be noted that equal amounts of both *cis*- and *trans*-Re(CO)$_4$(PBz$_3$)$_3$I were formed in this reaction. From the results obtained from the cleavage of $Re_2(CO)_9(PBz_3)/I_2$ with Br^- more trans monomer may have been expected. This suggests that, because of (i) steric factors and/or (ii) the more symmetrical nature of **6**, attack of an external nucleophile may also give rise to cis products. Although the details of this finding will have to be explored further the data again suggest that a maximum of 50% trans product is obtainable from the cleavage reaction.

It is further ascertained that the amount of Br_2 added to the reaction mixture can influence the product distribution. It was found that if 0.5–0.9 equiv of Br_2 was used in the cleavage of $Re_2(CO)_8(PBz_3)_2$ the expected 60/40 cis/trans product ratio was obtained (Table V). However, if *excess* Br_2 (0.1 equiv excess) was used then only the cis (100%) product was formed. The excess Br_2 could readily oxidize the Re monomers to yield 17- or 19-electron species. There is precedent in the literature for the catalytic role of odd electron metal carbonyl species in inducing cis–trans isomerization reactions[22] and this could explain the observed phenomenon. Indeed, *trans*-Re(CO)$_4$LI was observed to slowly isomerize to *cis*-Re(CO)$_4$LI at room temperature in C_6D_6 in the presence of Br_2. Interestingly, addition of *excess* I_2 to $Re_2(CO)_8(PBz_3)_2$ did not result in a change in the ratio of *cis*/*trans*-Re(CO)$_4$LX complexes. Thus the reaction of 0.5–1.1 equiv of I_2 with $Re_2(CO)_8(PBz_3)_2$ always gave a ~60:40 *cis*/*trans*-Re(CO)$_4$(PBz$_3$)I ratio.

Isomerization Kinetics. Qualitative data for the trans–cis isomerization reaction of Re(CO)$_4$LI were initially obtained from an NMR study required to ascertain the temperature range and types of L to use in our study.

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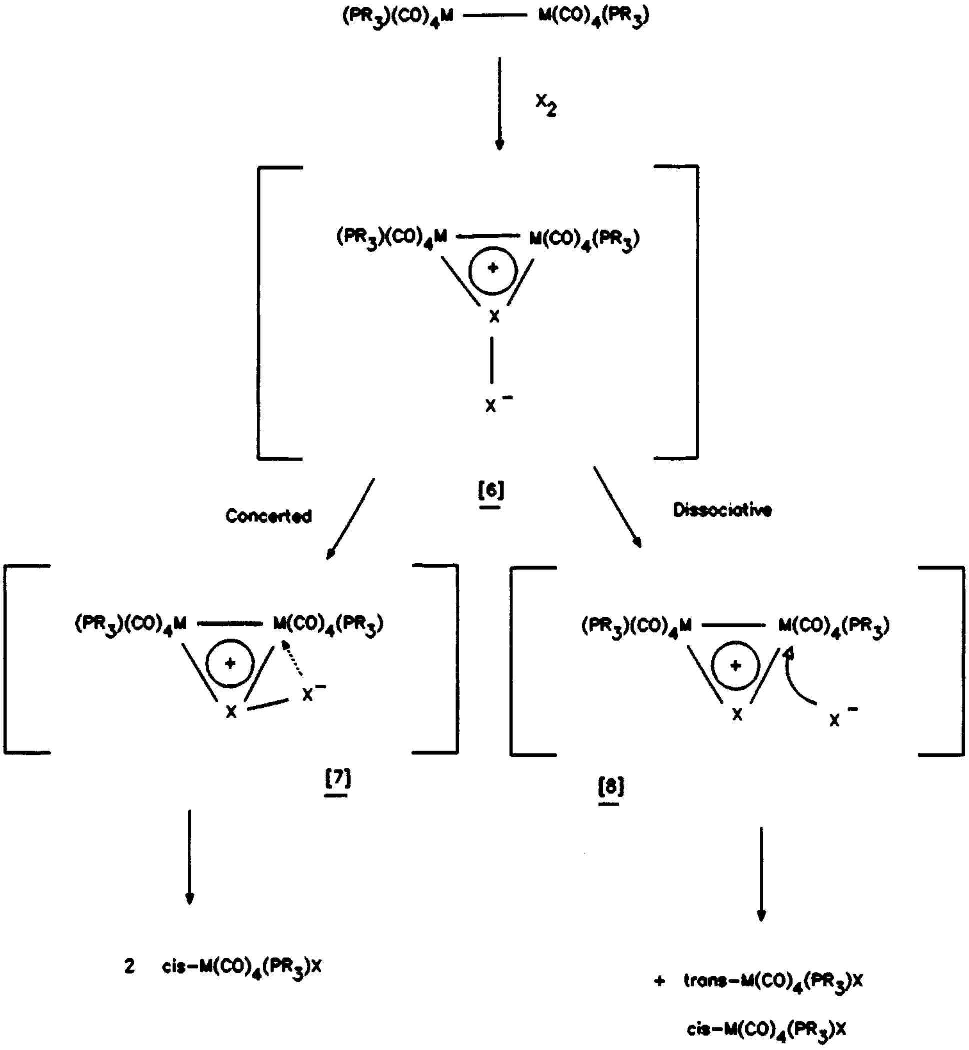
Scheme III. Cleavage of $Re_2(CO)_8(PR_3)_2$ with X_2



Kinetic data for the *trans*/*cis*-$Re(CO)_4LI$ (L = PPh_3, $P(O^iPr)_3$, $P(OPh)_3$, PMe_2Ph, $PMePh_2$, PBz_3, $P(O\text{-}o\text{-}tol)_3$) isomerization reaction were then obtained from reactions carried out in an IR cell set at a constant temperature. Our data are consistent with a first-order nondissociative process (good linear plots of ln $(A_\infty - A_t)$ vs t over 2 half-lifes). The rate constant data are shown in Table IX.

The kinetics and thermodynamics of isomerization of $Mo(CO)_4L_2$-type complexes (L = phosphines and phosphites) have been extensively studied. Both dissociative and intramolecular rearrangement mechanisms have been observed that depend to some extent on the ligand size. Thus thermolysis of $Mo(CO)_4L_2$ (L = PPh_3)[12j] results in cis–trans isomerization via a dissociative isomerization, while for $Mo(CO)_4L_2$ (L = PEt_3, P^nBu_3, PMe_3) isomerization occurs via an intramolecular trigonal prism twist mechanism with $\Delta H^{\ddagger} = 24.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5.6$ eu (L = P^nBu_3, PEt_3).[12b,k] For nondissociative isomerization the rate of isomerization was shown to increase with increase in ligand size.[12k] Similarly, complexes *trans*-$Mo(CO)_2(DP)_2$ (DP = bidentate phosphine ligands) isomerize via a nondissociative mechanism to the cis isomer with $\Delta H^{\ddagger} = 27.3 - 38.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -45 - 55$ eu.[12m]

Intramolecular rearrangements have also been shown to occur in the trans–cis isomerization of $W(CO)_4(CS)(^{13}CO)$ ($\Delta H^{\ddagger} = 31.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = 9.1$ eu) 20 times more rapidly than $CO/^{13}CO$ exchange in a ^{13}CO atmosphere.[12i] Cis–trans isomerization of $Ru(CO)_4(SiCl_3)_2$ also occurs via a nondissociative mechanism ($\Delta H^{\ddagger} = 24.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.9$ eu).[12h] The related osmium complex, $Os(CO)_4(SiMe_3)_2$, isomerized by a similar nondissociative mechanism with a lower activation energy ($\Delta H^{\ddagger} = 17.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = 1.6$ eu).[12h] The dicarbonyl-substituted complexes $Mn(CO)_3P_2Br$ (P = group-15 donor ligand) were shown to undergo cis–trans isomerization via a dissociative mechanism ($E_a = 26.4$–31.8 kcal mol^{-1}, $\Delta S^{\ddagger} = 3.0$–$14.3$ eu).[12e]

Since the literature values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for both the isomerization and dissociative pathways are similar, the mechanism cannot presently be ascertained from these measureable quantities. The accuracy of our data also does not permit an unequivocable evaluation of the reaction mechanism. However, isomerization of *trans*-$Re(CO)_4(PBz)_3I$ in the presence of added ligand does suggest that the major reaction pathway, for this specific reaction, occurs via a nondissociative pathway (see Experimental Section).

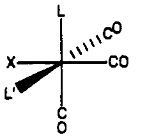
An analysis of the values obtained for the rate constant, k (90 °C, Table IX), reveals the relative isomerization rate order $P(O\text{-}o\text{-}tol)_3 < PBz_3 \sim P(OPh)_3 \sim PMe_2Ph < PMePh_2 \sim PPh_3 < P(O^iPr)_3 < P(OMe)_3$. No consistent trends relating the rates to steric or electronic effects associated with L are evident. Small electronic effects associated with L are evident. Little correlation is also noted between our data and qualitative data for the trans–cis isomerization reactions of $Mn(CO)_4LBr$.[2] However, if our data set is separated into the phosphine- and phosphite-containing complexes and small data sets are considered separately, trends become more evident.

(i) Phosphites: Steric effects do not appear to be dominant. Thus $P(OPh)_3$ and $P(O^iPr)_3$, which are approximately the same size[23] (128° and 130°, respectively), differ markedly in their rates. However, the trend observed shows some correlation with reported pK_a values[24] (an electronic effect). It is apparent that an *increase* in ligand basicity results in a *increase* in the isomerization reaction rate.

(ii) Phosphines: A different trend is observed within the set of phosphine ligands. Here PMe_2Ph, the more basic ligand, isomerizes more slowly than PPh_3. On steric grounds the complexes with the smaller ligand (PMe_2Ph, 122°; PPh_3, 145°) would be expected to isomerize more rapidly.

A more detailed kinetic study will be required to unravel the significance of these results.

Comparative Reactivities of *cis*- and *trans*-Re(CO)$_4$(PBz$_3$)I. Reactions of *cis*-Re(CO)$_4$LX (L = group-15 donor ligands, X = halide) with ligands L′ (group-15 donor ligands,[25] RNC[16]) lead to the synthesis of the two known isomers of $Re(CO)_3LL'X$, **9** and **10**. Although there are many reports in the literature on the synthesis and isomerization of these isomers,[12] there are no data available on the synthesis and properties of isomers **11** and **12**. This arises in part because of a lack of information available on the precursor to these types of complexes, namely, *trans*-Re(CO)$_4$LX,[10] which cannot be generated by classical reaction routes.



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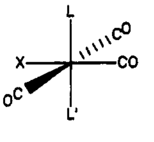

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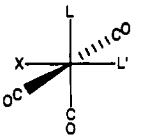

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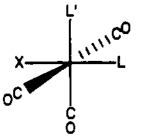

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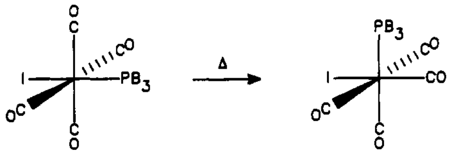
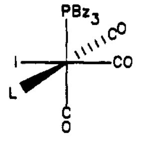


(13) (14)

We have therefore investigated the chemistry and properties of one member of the series, *trans*-Re(CO)$_4$LI, in which L is the bulky phosphine PBz$_3$, **13**, to abstract features of the chemistry of this class of complexes. **13** only slowly isomerizes to the cis complex **14** (see above), and, further, **13** and **14** can readily be differentiated by ^1H and ^{31}P NMR spectroscopy.

(a) Thermal Reactions. Reaction of *trans*-Re(CO)$_4$(PBz$_3$)I with L (L = $P(OPh)_3$, *t*-BuNC) in C_6D_6 at 100 °C for 90 min was monitored by NMR spectroscopy. Under these conditions *trans*/*cis*-Re(CO)$_4$(PBz$_3$)I isomerization occurs more readily (60%) than substitution. The products **15** and **16** were obtained in a 2:1 ratio (8% total). No isomers corresponding to **17** and **18** were detected. Phosphine substitution was also observed resulting in the formation of **19** (L = *t*-BuNC, 8%).



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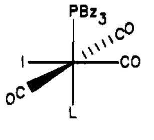

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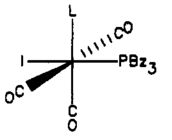

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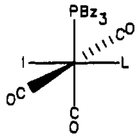

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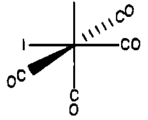
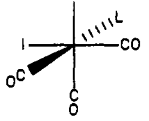
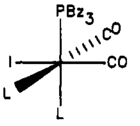


(19)



(20)



(21)

(b) Me$_3$NO-Induced Reaction. Reaction of *trans*-Re(CO)$_4$(PBz$_3$)I with Me$_3$NO results in the formation of three Re(CO)$_3$(PBz$_3$)LI complexes, **15a**, **16a**, and **17a** (L = CH_3CN) in a 22:2:1 ratio, as detected by ^1H and ^{31}P NMR spectroscopy. Isomers **15a** and **16a** were completely characterized by comparative IR and NMR spectroscopy. The third complex is believed to be isomer **17a**. Although prepared in low yield and not isolated, characterization of **17a** is based on the following:

(1) In the ^{31}P spectrum, the ^{31}P NMR resonance position (δ = 2.0 ppm) corresponds to that expected for a P ligand trans to I by comparison with NMR data for *trans*-Re(CO)$_4$(PBz$_3$)I (δ = 5.1 ppm).

(2) Heating a solution containing **15a**, **16a**, and **17a** (L = CH_3CN) in an NMR tube (80 °C, 45 min) results in the disappearance of only **17a**.

(3) Addition of *t*-BuNC to a solution containing **15a**, **16a**, and **17a** (L = CH_3CN) in an NMR tube and subsequent heating (80 °C) results only in the formation of isomers **15b** and **16b** (L = *t*-BuNC).

Of significance is the ratio 22:2:1 of isomers **15a**/**16a**/**17a** formed in the reaction of *trans*-Re(CO)$_4$LI with Me$_3$NO. This is to be contrasted with the major amount of trans isomer **16a** formed from reaction of *cis*-Re(CO)$_4$(PBz$_3$)I with Me$_3$NO (see Table VIII). This strongly suggests that little, if any, isomerization of *trans*-Re(CO)$_4$(PBz$_3$)I occurs prior to reaction with Me$_3$NO. Since isomerization of **16a** to **15a** is a slow process at room temperature (little change in the 1:2 ratio observed at 75 °C after 1 h in an NMR tube), the isomerization of **17a** to **15a** must occur by way of a transition state or intermediate that evenutally enables the PBz$_3$ ligand to occupy the site cis to I.

Both *cis*- and *trans*-Re(CO)$_4$(PBz$_3$)I were shown to react more slowly with CH_3CN than the related unsubstituted complex Re(CO)$_5$I. Thus, when an equimolar mixture of either *cis*- or *trans*-Re(CO)$_4$(PBz$_3$)I *and* Re(CO)$_5$I was reacted with Me$_3$NO the only substituted acetonitrile products obtained did not contain a phosphine ligand. The new products were identified as $Re(CO)_{5-x}(NCCH_3)_xI$ (x = 1, **19a**; x = 2, **20a**) by ^1H NMR spectroscopy and by

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conversion of the new products, after heating the reaction mixture in the presence of added *t*-BuNC, to the related known complexes $Re(CO)_{5-x}(CNBu\text{-}t)_xI$ ($x = 1, 2$).[16] It is thus apparent that the *phosphine ligand present in either cis- or trans-*$Re(CO)_4(PBz_3)I$ *deactivates the carbonyl ligands* to Me_3NO-induced decarbonylation, relative to the carbonyls in the unsubstituted complex, $Re(CO)_5I$.

(c) PdO-Catalyzed Reaction. Reaction of *cis*-$Re(CO)_4(PBz_3)I$ with *t*-BuNC in the presence of PdO at 100 °C in C_6D_6 gave isomers **15b** and **16b** in a 7:1 ratio (see Table VIII). A similar reaction but starting with *trans*-$Re(CO)_4(PBz_3)I$ gave four phosphorus-containing products, namely, isomers **15b** and **16b** as well as **17b** and the disubstituted product **21b** in a ratio of 8:5:1:6 (see Table VIII). The major change in product distribution in changing from the cis to the trans isomer confirms that the substitution reactions must occur prior to the isomerization reaction.

Competitive catalyzed substitution reactions of *cis*- or *trans*-$Re(CO)_4(PBz_3)I$ and $Re(CO)_5I$ with *t*-BuNC were also carried out (25 °C, C_6D_6). In both reaction mixtures the unsubstituted complex reacted more rapidly with RNC than the substituted complexes to give **19b** and **20b**. Thus no activation of the CO ligands when PBz_3 is trans to I is apparent. A reaction between a 1:1 mixture of *cis*- and *trans*-$Re(CO)_4(PBz_3)I$ and 0.5 equiv of *t*-BuNC was also performed. From the data (Table VIII) the *apparent* rates of CO substitution are similar. However, if it is assumed that the CO groups cis to L are more readily replaced than CO groups trans to X or L[11] then the trans complex reacts at half the rate of the cis complex (i.e., four equivalent carbonyls in the trans isomer versus two equivalent carbonyls in the cis isomer). This is an unexpected result. Consideration of the cis and trans isomers shows that the "reactive" CO groups in both compounds are mutually cis to I, PBz_3, and two CO ligands and trans to one CO ligand. The difference in reactivity must therefore relate to the cis or trans arrangement of the I and PBz_3 ligands.

The strong M–CO bonds in the trans complex are also manifested by an X-ray crystal structure determination of *trans*-$Re(CO)_4(PPh_3)I$.[26] The data reveal an average M–CO bond length of 1.971 (11) Å. This is the same as the cis,cis M–CO bond length data reported for *cis*-$Re(CO)_4(PEt_3)Cl$[27] (1.976 (12), 1.973 (13) Å), indicating similar M–CO bond strengthening in both *trans*-$Re(CO)_4LX$ and *cis*-$Re(CO)_4LX$ complexes.

Conclusion

Substitution reactions of $Re(CO)_5X$ invariably result in the synthesis of *cis*-$Re(CO)_4LX$ complexes. The synthesis of *trans*-$Re(CO)_4L$ complexes can be achieved by indirect routes via cleavage of the axially substituted dimer complexes. This study has shown that the complexes available by this route are dependent on the propensity of the ligands to occupy the axial positions in the parent dimer complexes. Further, the stability of the trans isomer obtained is dependent on the metal, ligand, and halide.

The dimer cleavage mechanism is proposed to consist of a number of independent pathways resulting invariably in mixtures of the cis and trans isomers. In addition the trans isomer is predicted to be obtained in a maximum 50% yield by this synthesis technique. The trans isomer is proposed to be formed via a dissociative pathway, by intermolecular attack of a halide nucleophile on the cationic bimetallic intermediate. The pure trans product can be isolated from the reaction mixture by fractional recrystallization in yields of 20–40%.

Isomerization of *trans*-$Re(CO_4)(PBz_3)I$ occurs more readily at elevated temperatures than CO substitution in the presence of $P(OPh)_3$ and *t*-BuNC. The rate of isomerization is dependent on the steric as well as the electronic properties of the ligand. PdO-catalyzed CO substitution requires elevated temperatures but results in more rapid substitution than isomerization. Low-temperature CO substitution can be induced by using the decarbonylating agent Me_3NO. The trans isomer exhibits a surprisingly low degree of CO substitution reactivity, reacting at a slower rate than the cis isomer.

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