

visible in an *E* map (MULTAN78), and all remaining atoms were located in subsequent difference Fourier synthesis. Hydrogen atoms were subsequently located and refined. While the positions of the hydrogen atoms are not well determined, they are qualitatively correct and converged properly. Refinement was blocked due to the large number of parameters.

A final difference Fourier was featureless, the largest peak being 0.45 e/Å<sup>3</sup>.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE-8219206) for support of this work.

**Registry No.** Ia, 95531-69-4; Ib, 95552-55-9; IIa, 94598-00-2; IIb, 95531-70-7; IIc, 95531-71-8; Zr(CH<sub>2</sub>Ph)<sub>4</sub>, 24356-01-2; Zr-(CH<sub>2</sub>PhF)<sub>4</sub>, 34072-35-0; 2,6-di-*tert*-butylphenol, 128-39-2; 2,6-di-*tert*-butyl-4-methoxyphenol, 489-01-0.

**Supplementary Material Available:** Listings of isotropic thermal parameters and fractional coordinates for Ia and Ic, fractional coordinates for hydrogen atoms for Ia and Ib, and anisotropic thermal parameters, bond distances and angles, and observed and calculated structure factors for Ia-c (62 pages). Ordering information is given on any current masthead page.

## The PdO-Catalyzed Reaction between [Re<sub>2</sub>(CO)<sub>10</sub>] and Isocyanides

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The reaction between [Re<sub>2</sub>(CO)<sub>10</sub>] and RNC (R = Me, *t*-Bu, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, C<sub>6</sub>H<sub>11</sub>, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) is catalyzed by PdO to yield the products [Re<sub>2</sub>(CO)<sub>10-n</sub>(CNR)<sub>n</sub>] (*n* = 1-3, R = *t*-Bu, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, C<sub>6</sub>H<sub>11</sub>; *n* = 1-4, R = Me, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) rapidly and in moderate to excellent yields. The reaction occurs via stepwise replacement of CO groups and mixed-isocyanide derivatives can thus be synthesized, e.g., [Re<sub>2</sub>(CO)<sub>8</sub>(CNBu-*t*)-(CNC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)]. The products have been completely characterized by IR and NMR spectroscopy and for certain derivatives by mass spectrometry. A correlation between the above spectroscopic parameters and the product geometry, after crystallographic determination of the structures of pertinent substituted derivatives, has been made. In all products the isocyanide ligands occupy *cis* equatorial positions on either the same or different Re atoms, indicating the dominance of electronic rather than steric factors in the control of the final product geometry. Labeling studies using [Re(<sup>13</sup>CO)<sub>12</sub>] indicate that the PdO-catalyzed reaction to yield [Re<sub>2</sub>(CO)<sub>9</sub>(CNBu-*t*)] occurs via a CO dissociative mechanism rather than a process involving metal-metal bond cleavage.

### Introduction

Transition-metal cluster complexes in both high and low oxidation states have been actively studied since the early 1960s.<sup>1</sup> Part of the justification for this activity has arisen from the suggestion that metal clusters can be viewed as bridges between molecular and solid-state chemistry<sup>2</sup> and further that cluster catalysis might give information on multi-atom (surface) catalysis.<sup>3</sup> As a prerequisite to establishing whether the above hypotheses are justified a fundamental understanding of the chemistry of cluster reactions is required and is being developed.<sup>4</sup>

Some years ago we commenced a study of the substitution reactions of [M<sub>2</sub>(CO)<sub>10</sub>] (M<sub>2</sub> = Mn<sub>2</sub>, Re<sub>2</sub>, MnRe) using catalysts to induce CO displacement by phosphines and isocyanide ligands.<sup>5</sup> This system was chosen as a model for an investigation of the chemical reactivity of larger clusters (trimers, tetramers, etc.) as it contains one M-M bond and no bridging ligands (in the ground state).<sup>6</sup>

Further, the use of catalysts could allow for the synthesis of [M<sub>2</sub>(CO)<sub>10-n</sub>L<sub>n</sub>] (*n* > 1) complexes under conditions in which M-M bond cleavage is eliminated or greatly reduced. Indeed, when this study was commenced, the mechanism of the thermal substitution reaction [Mn<sub>2</sub>(CO)<sub>10</sub> + PPh<sub>3</sub> → [Mn<sub>2</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)] + CO was postulated to occur via Mn-Mn bond cleavage rather than a CO dissociative process<sup>8</sup> and it was anticipated that a lower temperature catalytic pathway would eliminate the possibility of the Mn-Mn cleavage route. (Recent labeling and other studies<sup>9</sup> have, however, now indicated that the thermal, high-temperature reaction occurs via a dissociative mechanism.)

This publication describes the catalyzed synthesis of a series of [Re<sub>2</sub>(CO)<sub>10-n</sub>(CNR)<sub>n</sub>] (*n* = 1-4; R = alkyl and aryl isocyanide) complexes from [Re<sub>2</sub>(CO)<sub>10</sub>] and RNC. Although the analogous Mn derivatives have been studied,<sup>10</sup> only one previous report of an analogous Re-RNC complex—a brief mention of the Raman spectrum of [Re<sub>2</sub>(CO)<sub>9</sub>(CNMe)]—has been made.<sup>11</sup> These Re and Mn complexes are of particular interest as it is hoped that the stereochemistry of the substituted products will eventually

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Table I. Catalyst Testing on the Reaction  $[\text{Re}_2(\text{CO})_{10}] + t\text{-BuNC} \rightarrow [\text{Re}_2(\text{CO})_9(\text{CNBu-}t)]^a$ 

catalyst <sup>b</sup>	reactn time, min
blank	210 <sup>c</sup>
PdO	<1
Pd/C (10%)	105
Pd/C (5%)	120
Pd/CaCO <sub>3</sub> (10%)	<1
Pd/BaCO <sub>3</sub> (5%)	6
Pd/BaSO <sub>4</sub> (5%)	130
Pd/Al <sub>2</sub> O <sub>3</sub> (5%)	5
Pt/Al <sub>2</sub> O <sub>3</sub> (5%)	70
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$	40
Pd impregnated polymer (40 mesh)	105

<sup>a</sup> See Experimental Section for experimental procedure.

<sup>b</sup> No catalysis was observed for the following: CoCl<sub>2</sub>·2H<sub>2</sub>O, IrCl<sub>3</sub>·nH<sub>2</sub>O, Zn, K<sub>2</sub>PtCl<sub>4</sub>, Pt/C (5 or 10%), Rh/C (5%), Ru/C (5%), Re/C (5%), PtBr<sub>2</sub>, and PtO<sub>2</sub>. <sup>c</sup> Under normal laboratory light; no reaction in the dark.

provide information on the stereochemistry of larger substituted clusters. Attempts to correlate structure with IR, NMR, and mass spectrometry have thus been made in this work and in particular a series of X-ray crystal structures determinations of selected Re–CNR derivatives have been ascertained.<sup>12</sup> A preliminary report on the X-ray crystal structure of  $[\text{Re}_2(\text{CO})_9(\text{CNBu-}t)]$  has been published.<sup>13</sup> These complexes also provide for the possibility of investigating the effect of (1) ligand donor/acceptor properties and (2) systematic CO substitution, on parameters such as M–M bond length,  $\nu(\text{M–M})$ , etc.,<sup>14</sup> information not readily available in the literature.

### Experimental Section

$[\text{Re}_2(\text{CO})_{10}]$  was purchased from Strem Chemicals and the PdO from Johnson Matthey Chemicals Ltd. MeNC was prepared by the literature method, and the other isocyanides were purchased from Fluka AG (*t*-BuNC and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC) or Merck (C<sub>6</sub>H<sub>11</sub>NC and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NC). Column chromatography was performed on silica gel (Merck 60F, 70–230 mesh) on 1 cm × 20 cm columns. Preparative TLC was performed on 20 × 20 cm silica gel plates of 250 μm layer thickness purchased from Merck Chemicals. All reactions were routinely carried out under nitrogen in degassed solvents.

Infrared spectra were recorded on a Pye-Unicam SP300 or Bruker IFS 85 FTIR spectrometer, NMR spectra on a Bruker WP80 FTNMR spectrometer, and mass spectra on a Varian MAT CH5 spectrometer operating at 70 eV. Melting points were recorded on a Köfler micro hot-stage apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratories, CSIR, Pretoria.

**Catalyst Testing.**  $[\text{Re}_2(\text{CO})_{10}]$  (0.2 mmol) and potential catalyst (4 mg) were stirred in benzene (4 mL) at 55 °C. *t*-BuNC (0.22 mmol) was then added to the stirred solution and the progress of the reaction monitored by TLC (silica gel, eluent hexane–benzene (20%)). The reaction times listed in Table I correspond to the complete conversion of  $[\text{Re}_2(\text{CO})_{10}]$  to  $[\text{Re}_2(\text{CO})_9(\text{CNBu-}t)]$ , as detected by TLC.

**PdO-Catalyzed Synthesis of  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  ( $n = 1-3$ , R = *t*-Bu, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, C<sub>6</sub>H<sub>11</sub>;  $n = 1-4$ , R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Me).**  $[\text{Re}_2(\text{CO})_{10}]$  (1.0 mmol) and the catalyst PdO (20 mg) were stirred in toluene (10 mL). RNC ( $n$  mmol) was then added to the solution, and the reaction was monitored by TLC (silica gel, eluent hexane–benzene (20% or 30%)). The reaction was terminated when complete conversion of  $[\text{Re}_2(\text{CO})_{10}]$  to  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  had occurred or when no further reaction could be detected by

Table II. Reaction Conditions and Product Yields for the PdO-Catalyzed Syntheses of the Complexes  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]^a$ 

R	n	T, °C	t, min	yield, <sup>b</sup> %
<i>t</i> -Bu	1	55	1	98
	2	55	5	80
	3	55	45	80
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	1	55	1	75
	2	80	5	75
	3	80	45	85
C <sub>6</sub> H <sub>11</sub>	1	55	1	80
	2	110	15	70
	3	110	60	75
2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1	55	5	70
	2	80	20	70
	3	110	40	98
	4	110	150	40
Me	1	55	10	80
	2	110	15	80
	3	110	30	80
	4	110	150	20

<sup>a</sup> Catalyst/substrate ratio ≈ 1/6. <sup>b</sup> Isolated yield.

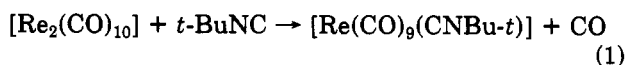
TLC. Column chromatography (Silica gel, eluent hexane–benzene (20%)) gave the required products in the indicated yields (Table II). Recrystallization under nitrogen from solutions of dichloromethane–hexane or benzene–hexane gave the products as white or yellow crystalline solids. In the case of the C<sub>6</sub>H<sub>11</sub>NC derivatives ( $n = 1-3$ ), yellow oils were obtained, which on standing solidified over a period of several months. Analytical data for the new complexes is given in Table III.

**PdO-Catalyzed Synthesis of  $[\text{Re}_2(\text{CO})_9(\text{CNBu-}t)-(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$ .**  $[\text{Re}_2(\text{CO})_{10}]$  (1.0 mmol) and PdO (20 mg) were stirred in benzene (10 mL) at 55 °C. RNC (1 mmol, R = *t*-Bu or 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) was then added to the solution, and the reaction was monitored by TLC (silica gel, eluent hexane–benzene (30%)). After conversion of the  $[\text{Re}_2(\text{CO})_{10}]$  to  $[\text{Re}_2(\text{CO})_9(\text{CNR})]$  was judged (by TLC) to be complete, R'NC (1 mmol, R' = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> or *t*-Bu) was added. The reaction was terminated once all the  $[\text{Re}_2(\text{CO})_9(\text{CNR})]$  had been converted to  $[\text{Re}_2(\text{CO})_9(\text{CNR})_2]$ . The product  $[\text{Re}_2(\text{CO})_9(\text{CNBu-}t)-(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$  was isolated by using the same procedure as that for the  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  derivatives (see above) and recrystallized from dichloromethane–hexane solution to give a yellow crystalline solid (70% yield).

**PdO-Catalyzed Reaction of  $[\text{Re}_2(\text{CO})_{10}]$  and  $[\text{Re}_2(^{13}\text{C})_{10}]$  with *t*-BuNC (1:1 Ratio).**  $[\text{Re}_2(\text{CO})_{10}]$  (0.015 mmol),  $[\text{Re}_2(^{13}\text{C}-\text{O})_{10}]$  (0.015 mmol), and catalyst PdO (10 mg) were stirred in benzene at 50 °C. (The reaction vessel was foil-wrapped to exclude all light.) *t*-BuNC (0.031 mmol) was then added to the solution, and the reaction was monitored by TLC (silica gel, eluent hexane–benzene (10%)). The reaction to  $[\text{Re}_2(\text{CO})_9(\text{CNBu-}t)]$  was complete in less than 1 min, and the heating was stopped after 5 min. The product was isolated by preparative thin-layer chromatography (eluent hexane–benzene (10%)), extracted with dichloromethane, and recrystallized from dichloromethane–pentane solution, to give a white material,  $[\text{Re}_2(\text{CO})_9(\text{CNBu-}t)]$  (90% isolated yield).

### Results and Discussion

**Catalyst Testing.** Reaction 1 was chosen to screen potential catalysts for activity and the results of a portion of this study are given in Table I. This reaction was chosen as the test reaction since it can readily be monitored by TLC and the product is air stable.



Under normal laboratory lighting conditions reaction 1, in benzene at 55 °C, was found to give  $[\text{Re}_2(\text{CO})_9(\text{CNBu-}t)]$  in quantitative yield (210 min).<sup>13</sup> However, in the dark or in artificial laboratory light with total exclusion of

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Table III. Analytical Data for the  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  ( $n = 1-4$ ) Complexes

	color	mp, °C	elemental anal. <sup>a</sup>		
			C	H	N
$[\text{Re}_2(\text{CO})_9(\text{CNBu}-t)]$	white	104-106	23.6 (23.8)	1.2 (1.3)	1.9 (2.0)
$[\text{Re}_2(\text{CO})_9(\text{CNCH}_2\text{C}_6\text{H}_5)]$	yellow	66-67	27.9 (27.5)	0.98 (0.95)	2.0 (1.9)
$[\text{Re}_2(\text{CO})_9(\text{CNC}_6\text{H}_{11})]$	white	60-61	26.4 (26.2)	1.4 (1.5)	2.0 (1.9)
$[\text{Re}_2(\text{CO})_9(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$	cream	108-110	28.4 (28.6)	1.2 (1.2)	1.9 (1.9)
$[\text{Re}_2(\text{CO})_9(\text{CNMe})]$	yellow	104-106	20.1 (19.9)	0.41 (0.45)	1.8 (2.1)
$[\text{Re}_2(\text{CO})_8(\text{CNBu}-t)_2]$	white	94-97	28.6 (28.3)	2.3 (2.4)	4.1 (3.7)
$[\text{Re}_2(\text{CO})_8(\text{CNCH}_2\text{C}_6\text{H}_5)_2]$	yellow	73-75	34.9 (34.4)	1.7 (1.7)	3.5 (3.4)
$[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_{11})_2]$	yellow	42-44	32.6 (32.4)	2.7 (2.7)	3.4 (3.4)
$[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_2]$	yellow	173-174	36.2 (36.4)	1.9 (2.1)	3.3 (3.3)
$[\text{Re}_2(\text{CO})_8(\text{CNMe})_2]$	yellow	121-124	21.6 (21.2)	0.92 (0.89)	4.3 (4.1)
$[\text{Re}_2(\text{CO})_8(\text{CNBu}-t)(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$	yellow	106-108	32.4 (32.6)	2.2 (2.2)	3.5 (3.5)
$[\text{Re}_2(\text{CO})_7(\text{CNBu}-t)_3]$	white	150-152	33.5 (32.3)	3.5 (3.3)	5.2 (5.1)
$[\text{Re}_2(\text{CO})_7(\text{CNCH}_2\text{C}_6\text{H}_5)_3]$	yellow	115-116	40.3 (40.5)	2.3 (2.3)	4.6 (4.6)
$[\text{Re}_2(\text{CO})_7(\text{CNC}_6\text{H}_{11})_3]$	yellow	44-46	38.4 (37.5)	3.7 (3.7)	4.7 (4.7)
$[\text{Re}_2(\text{CO})_7(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_3]$	yellow	164-166	41.6 (42.3)	4.1 (4.4)	2.8 (3.1)
$[\text{Re}_2(\text{CO})_6(\text{CNMe})_4]$	yellow	143-144	22.5 (22.6)	1.2 (1.3)	5.9 (6.0)
$[\text{Re}_2(\text{CO})_6(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_4]$	yellow	201-202	42.2 (42.4)	3.4 (3.4)	5.3 (5.3)
$[\text{Re}_2(\text{CO})_6(\text{CNMe})_4]$	yellow	201-204	24.3 (23.9)	1.5 (1.7)	7.8 (8.0)

<sup>a</sup> Found (calculated values in parentheses).

Table IV. Reaction Times at 55 °C for the Uncatalyzed and PdO-Catalyzed Reaction  $[\text{Re}_2(\text{CO})_{10}] + \text{RNC} \rightarrow [\text{Re}_2(\text{CO})_9(\text{CNR})] + \text{CO}$ 

R	reaction time, min	
	uncatalyzed <sup>a</sup>	PdO catalyzed
<i>t</i> -Bu	210	<1
$\text{C}_6\text{H}_5\text{CH}_2$	360 <sup>b</sup>	<1
$\text{C}_6\text{H}_{11}$	180	<1
2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	360 <sup>b</sup>	5
Me	120	10

<sup>a</sup> Under normal laboratory light. <sup>b</sup> Reaction incomplete.

sunlight, no reaction occurs. No attempt to elucidate this thermal light induced uncatalyzed reaction has been made, but the reaction presumably occurs by fission of either the Re-Re or Re-CO bond.<sup>15</sup>

Reagents which have shown catalytic behavior in previous studies<sup>16</sup> were chosen for study, and as recorded in Table I the Pd reagents generally showed highest catalytic activity. Unfortunately it is not possible to relate the catalytic activity to the catalyst support as the surface area of the various Pd-supported reagents is not known. This is made apparent by the results on the use of 5% and 10% Pd on carbon (Pd/C) supports that give very similar reaction times (Table I). It is to be noted that neither  $\text{CaCO}_3$  nor activated carbon, i.e., the supports, catalyze reaction 1. An attempt to use reducing agents as catalysts,<sup>16</sup> e.g.,  $\text{LiAlH}_4$ , was unsuccessful. However, addition of PtO (to  $[\text{Re}_2(\text{CO})_{10}]/t\text{-BuNC}$ ) to remove traces of oxygen, followed by addition of  $\text{LiAlH}_4$  did result in catalysis (15 min). The results were unfortunately dependent on factors such as the order of reagent addition, oxygen, and light, and the complexity of the reaction did not warrant further investigation for our purposes.

From the results in Table I PdO was chosen as the catalyst for the investigation of the synthesis of  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  ( $n = 1-4$ ) derivatives. Reaction 1, in the presence of PdO, was found to be independent of sunlight, and consequently it was not found necessary to wrap re-

action flasks in foil to exclude light during the catalyzed reactions.

**The Catalyzed Reaction of  $[\text{Re}_2(\text{CO})_{10}]$  and Isocyanides.** The results of the study using PdO as catalyst are given in Tables II and IV. The data indicate that a substantial improvement in reaction rate is observed on the use of catalysts relative to the noncatalyzed reaction and that high isolated yields of products can generally be obtained under moderate reaction conditions. The only other report of the direct (photochemical) reaction between  $[\text{Re}_2(\text{CO})_{10}]$  and RNC (R = Me) did not indicate reaction times or product yields<sup>11</sup> and so no comparison of our method with the earlier values can be given.

Owing to the facile nature of the PdO-catalyzed synthesis of  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  ( $n = 1, 2$ ) some  $[\text{Re}_2(\text{CO})_{10-n+1}(\text{CNR})_{n+1}]$  is also found in the reaction. This accounts for the less than quantitative yields sometimes obtained. The products are, however, readily purified by column chromatography.

As the degree of substitution of  $[\text{Re}_2(\text{CO})_{10}]$  by RNC increases the reaction time to bring about the substitution also increases. Tetrasubstituted derivatives  $[\text{Re}_2(\text{CO})_6(\text{CNR})_4]$  could only be synthesized for R = Me and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and even then only in poor yields after long reaction times. The ability to achieve the highest degree of substitution for the latter two isocyanides could be related to the superior  $\pi$ -acceptor ability of aromatic isocyanides<sup>17</sup> (relative to aliphatic isocyanides) and to the small size of the MeNC ligand.<sup>18</sup> Attempts to prepare  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  with  $n > 4$  were unsuccessful. Reaction of  $[\text{Re}_2(\text{CO})_6(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_4]$  with excess isocyanide did yield a maroon solid with complex <sup>1</sup>H NMR and IR spectra ( $\text{CHCl}_3$ , 2085 (sh), 2060 (s), 1995 (sh), 1975 (ms), 1895 (sh), 1870 (m)  $\text{cm}^{-1}$ ) but with analytical data not in keeping with the pentasubstituted product formulation.

Since the complex  $[\text{Re}_2\{\text{P}(\text{OMe})_3\}_{10}]$  has been synthesized by indirect methods,<sup>19</sup> it seems that the restriction of the degree of substitution of  $[\text{Re}_2(\text{CO})_{10}]$  is electronic rather than steric in origin (cf. cone angle for  $\text{P}(\text{OMe})_3 = 107^\circ$ <sup>20</sup>). This is supported by an X-ray structure determination of  $[\text{Re}_2(\text{CO})_6(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_4]$ <sup>12</sup> which reveals two cis

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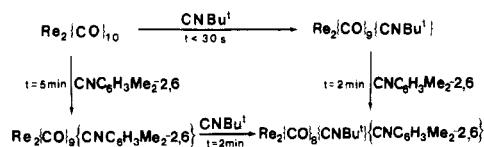
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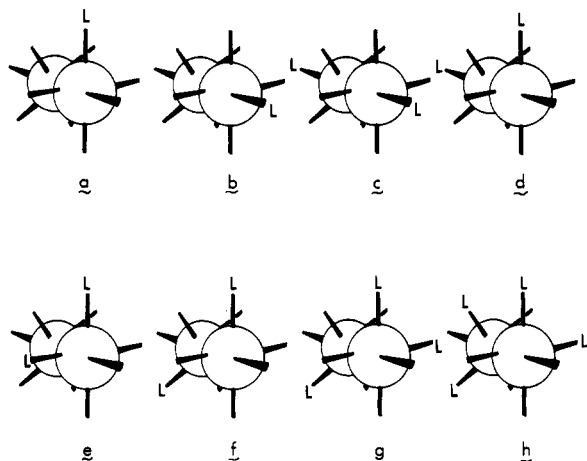
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**Figure 1.** Reaction scheme for the synthesis of the mixed-isocyanide complex  $[\text{Re}_2(\text{CO})_8(\text{CNBu}^t)(\text{CNC}_6\text{H}_4\text{Me}_2,6)]$ . The NMR data suggest that this complex could comprise a mixture of isomers.

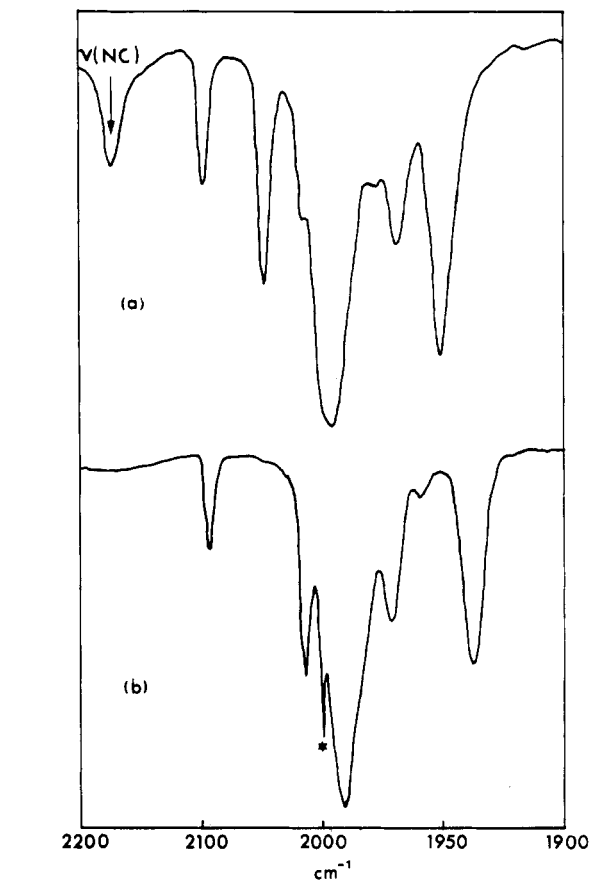


**Figure 2.** Possible geometries of some of the  $[\text{Re}_2(\text{CO})_{10-n}(\text{L})_n]$  (e.g.,  $\text{L} = \text{RNC}$ ;  $n = 1-4$ ) isomers. Note the 1,1-ax,eq- and 1,1-cis-dieq-disubstituted isomers are not shown.

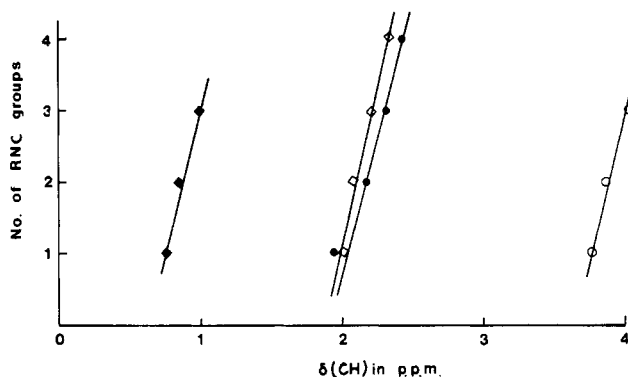
equatorial isocyanides on each Re atom. Since RNC ligands are weaker  $\pi$ -acceptor ligands than CO,<sup>17</sup> the CO group trans to RNC is less labile than that trans to another CO group.<sup>21</sup> A fifth RNC group would thus have to go trans to another RNC group or trans to the Re-Re bond, both electronically unfavorable situations.<sup>22,23</sup> It is to be noted that pentasubstituted derivatives have been synthesized by *indirect* methods, e.g.,  $[\text{Mn}_2(\text{CO})_5(\text{CNR})_5]$  ( $\text{R} = \text{Me}, \text{C}_6\text{H}_5, p\text{-ClC}_6\text{H}_4$ ) has been prepared by nucleophilic attack of  $[\text{Mn}(\text{CO})_5]^-$  on  $[\text{Mn}(\text{CNR})_5\text{X}]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{CN}$ ).<sup>24</sup>

Since the catalytic reaction of  $[\text{Re}_2(\text{CO})_{10}]$  with RNC proceeds in a quantitative and stepwise manner, the degree of substitution can be controlled by the number of equivalents of RNC added. It is thus possible to prepare mixed-isocyanide derivatives by adding different isocyanides sequentially. The order in which the different isocyanides is added is not important, and the same product can be obtained from the different routes, as indicated in Figure 1.

**Infrared Spectra.** IR data for the  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  ( $n = 1-4$ ) compounds are given in Table V, and as can be seen the compounds have complex spectra. The monosubstituted  $[\text{M}_2(\text{CO})_9\text{L}]$  complexes ( $\text{M} = \text{Mn}, \text{Re}$ ) can exist in only two different geometries with the L group occupying either an axial or equatorial position relative to the M-M bond (Figure 2a,b). Group theory predicts five  $\nu(\text{CO})$  IR-active absorptions for the *ax*- $[\text{M}_2(\text{CO})_9\text{L}]$  isomer (point group  $C_{4v}$ ) and nine  $\nu(\text{CO})$  absorptions for the *eq*- $[\text{M}_2(\text{CO})_9\text{L}]$  isomer (point group  $C_2$ ). However, many *eq*- $[\text{M}_2(\text{CO})_9\text{L}]$  complexes reported in the literature<sup>25</sup> have less absorptions than expected, no doubt due to band overlap. The IR spectrum of  $[\text{Re}_2(\text{CO})_9(\text{CNR})]$  has one



**Figure 3.** IR spectra in the  $\nu(\text{CO})$  region for (a)  $[\text{Re}_2(\text{CO})_9(\text{CNBU}^t)]$  and (b)  $[\text{Mn}_2(\text{CO})_9(\text{PMe}_2\text{Ph})]$  (\*spectrometer grating change).



**Figure 4.** NMR data for the  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  ( $n = 1-4$ ) complexes. The figure indicates the linear relationship between the resonance of the  $\text{CH}_x$  group of the isocyanide against the degree of substitution:  $\blacklozenge$ ,  $\text{RNC} = t\text{-BuNC}(\text{CH}_3)$ ;  $\diamond$ ,  $\text{RNC} = \text{MeNC}(\text{CH}_3)$ ;  $\bullet$ ,  $\text{RNC} = 2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}(\text{CH}_3)$ ;  $\circ$ ,  $\text{RNC} = \text{C}_6\text{H}_5\text{CH}_2\text{NC}(\text{CH}_2)$ .

$\nu(\text{NC})$  and six or seven  $\nu(\text{CO})$  absorptions, not inconsistent with the expected *eq*- $[\text{Re}_2(\text{CO})_9(\text{CNR})]$  geometry. However a comparison of the IR spectrum of  $[\text{Re}_2(\text{CO})_9(\text{CNBU}^t)]$  with that of *ax*- $[\text{Mn}_2(\text{CO})_9(\text{PMe}_2\text{Ph})]$ ,<sup>26</sup> a structure unequivocally determined by X-ray crystallography,<sup>27</sup> indicates that the IR spectra are remarkably similar (Figure 3). A crystal structure determination of  $[\text{Re}_2(\text{CO})_9(\text{CNBU}^t)]$  was thus undertaken, and this re-

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Table V. Spectroscopic Data for the Complexes  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  ( $n = 1-4$ )

Complex	IR, $\sigma, \nu \text{ cm}^{-1}$			NMR, $\delta$		
	$\nu(\text{CO})$	$\nu(\text{NC})$	$\nu(\text{CO})$	$\text{CH}_3, \text{CH}_2, \text{or } \text{C}_6\text{H}_{11}$	$\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5$
$[\text{Re}_2(\text{CO})_8(\text{CNBu-t})]$	2050 (m)	2101 (m)	1996 (vs)	1970 (m)	1952 (s)	0.75
$[\text{Re}_2(\text{CO})_8(\text{CNCH}_2\text{C}_6\text{H}_5)]$	2050 (m)	2100 (m)	1997 (vs)	1971 (m)	1954 (s)	3.77
$[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_{11})]$	2050 (m)	2102 (m)	1997 (vs)	1970 (m)	1952 (s)	1.05-1.25, <sup>d</sup> 0.82-0.97 <sup>d</sup>
$[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$	2048 (m)	2090 (m)	2000 (vs)	1974 (m)	1955 (s)	2.00
$[\text{Re}_2(\text{CO})_8(\text{CNMe})]$	2053 (m)	2105 (m)	1998 (vs)	1972 (m)	1955 (s)	1.94
$[\text{Re}_2(\text{CO})_8(\text{CNBu-t})]$	1978 (vs)	2060 (w)	1935 (s)	...	...	0.89
$[\text{Re}_2(\text{CO})_8(\text{CNCH}_2\text{C}_6\text{H}_5)]$	2031 (m)	2066 (w)	1939 (s)	...	...	3.87
$[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_{11})]$	1979 (vs)	2064 (m)	1922 (w)	...	...	0.85, 0.90, 1.09, 1.26 <sup>d</sup>
$[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_2]$	1984 (vs)	2055 (m)	1940 (m)	...	...	2.10
$[\text{Re}_2(\text{CO})_6(\text{CNMe})_2]$ <sup>e</sup>	1980 (vs)	2072 (w)	1922 (m)	...	...	2.10, 2.16 <sup>g</sup>
$[\text{Re}_2(\text{CO})_6(\text{CNBu-t})]$	1982 (vs)	2059 (m)	1939 (s)	...	...	0.86, 2.10, 2.14 <sup>g</sup>
$[\text{Re}_2(\text{CO})_7(\text{CNMe}-2,6)]$	1987 (vs)	2030 (w)	1924 (w)	...	...	0.98, 1.02 <sup>f</sup>
$[\text{Re}_2(\text{CO})_7(\text{CNBu-t})]$	1992 (vs)	2039 (m)	1963 (vs)	...	...	4.02, 4.05 <sup>f</sup>
$[\text{Re}_2(\text{CO})_7(\text{CNCH}_2\text{C}_6\text{H}_5)]$ <sup>e</sup>	1990 (vs)	2032 (m)	1927 (m)	...	...	0.89, 0.93, 1.40 <sup>d</sup>
$[\text{Re}_2(\text{CO})_7(\text{CNC}_6\text{H}_{11})]$	1990 (vs)	2033 (m)	1929 (sh)	...	...	2.18, 2.23 <sup>f</sup>
$[\text{Re}_2(\text{CO})_7(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$ <sup>e</sup>	1980 (vs)	2060 (w)	1929 (sh)	...	...	2.25, 2.31 <sup>f</sup>
$[\text{Re}_2(\text{CO})_7(\text{CNMe})_2]$ <sup>e</sup>	1980 (vs)	2040 (w)	1919 (sh)	...	...	2.34
$[\text{Re}_2(\text{CO})_7(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$ <sup>e</sup>	1944 (m)	1978 (vs)	1891 (m)	...	...	2.45
$[\text{Re}_2(\text{CO})_6(\text{CNMe})_4]$ <sup>e</sup>	1880 (m)	1971 (vs)	1880 (m)	...	...	...

<sup>a</sup> Recorded in hexane unless otherwise stated. <sup>b</sup> sh = shoulder; w = weak; m = medium; s = strong; vs = very strong. <sup>c</sup> Recorded in  $\text{C}_6\text{D}_6$  relative to  $\text{Me}_4\text{Si}$ . <sup>d</sup> Multiplet. <sup>e</sup> Recorded in chloroform. <sup>f</sup> Ratio 2:1. <sup>g</sup> Ratio 5:1.

vealed that the RNC ligand did occupy an equatorial position relative to the Re-Re bond.<sup>13</sup> It is thus apparent that care must be applied when relating IR spectra to geometry for  $[\text{M}_2(\text{CO})_8\text{L}]$  complexes.

The disubstituted complex  $[\text{M}_2(\text{CO})_8(\text{CNR})_2]$  can exist as three possible isomer types, viz., ax-ax, ax-eq, and eq-eq. The diaxial isomer (Figure 2c) is ruled out by IR spectroscopy as only two  $\nu(\text{CO})$  absorptions are predicted by group theory (point group  $D_{4d}$ ), as has indeed been observed for the *diax*- $[\text{M}_2(\text{CO})_8(\text{PR}_3)_2]$  ( $\text{M} = \text{Mn}, \text{PR}_3 = \text{PMePh}_2$ ,<sup>28</sup>  $\text{M} = \text{Re}, \text{PR}_3 = \text{PMe}_2\text{Ph}^{12}$ ) complexes, whose structures have been determined by X-ray crystallography. Table V indicates that four or five  $\nu(\text{CO})$  bands are observed in the IR spectra of the  $[\text{Re}_2(\text{CO})_8(\text{CNR})_2]$  complexes. For the remaining geometries the two ligands can be on the same or different metal atoms (Figure 2e,f). These isomers are predicted to have eight  $\nu(\text{CO})$  absorptions. Although the ax-eq isomers can be eliminated on electronic grounds, it is still not possible to relate the substitution geometry (Figure 2e or f) to the IR spectrum without prior knowledge of the product geometry. It is also to be noted that for the e isomer different conformers are also possible, but it is unlikely that these will be detected by IR spectroscopy.

X-ray crystallographic studies of  $[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_4\text{Me}_2-2,6)_2]$ <sup>12</sup> and  $[\text{Mn}_2(\text{CO})_8(\text{CNBu-t})_2]$ <sup>29</sup> were thus undertaken to establish the respective isomer geometries. Both structures indicated the expected eq-eq geometry, but the Re complex contained isocyanides on different atoms (i.e., 1,2-*cis-dieq*- $[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_2]$ ) (the numbers 1 and 2 refer to the Re atoms) while the Mn complex was shown to be the 1,1-*cis-dieq*- $[\text{Mn}_2(\text{CO})_8(\text{CNBu-t})_2]$  isomer. The IR spectra of these complexes are quite different and thus allow for isomer identification from IR spectra.

It is interesting to note that the IR spectrum of a polycrystalline sample of  $[\text{Mn}_2(\text{CO})_8(\text{CNBu-t})_2]$  is a superposition of the spectra of the 1,1- and 1,2-*dieq* isomers with the 1,2 isomer predominating.<sup>10</sup> These mixtures had been predicted from NMR spectroscopy.<sup>10</sup> The  $[\text{Re}_2(\text{CO})_8(\text{CNR})_2]$  complexes by contrast give no indication in their IR or NMR spectra of the formation of the 1,1 isomer (MeNC may be an exception; see below).

All the other  $[\text{Re}_2(\text{CO})_8(\text{CNR})_2]$  complexes have IR spectra similar to that of  $[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_2]$ .

For  $[\text{M}_2(\text{CO})_7(\text{CNR})_3]$  complexes only geometries with three equatorial RNC groups are considered as likely (see above) and seven  $\nu(\text{CO})$  absorptions are predicted for this isomer type, irrespective of the conformer geometry. The  $[\text{Re}_2(\text{CO})_7(\text{CNR})_3]$  complexes synthesized have four to six  $\nu(\text{CO})$  bands and one or two  $\nu(\text{NC})$  bands in their IR spectra. A crystal structure determination of  $[\text{Re}_2(\text{CO})_7(\text{CNMe})_3]$  has confirmed the 1-eq, 2,2-*cis-dieq* geometry<sup>12</sup> (Figure 2g).

The tetrasubstituted derivative is also expected to have all four ligands in equatorial positions and group theory predicts six  $\nu(\text{CO})$  bands for both the staggered and eclipsed conformers. The complexes  $[\text{Re}_2(\text{CO})_6(\text{CNR})_4]$  ( $\text{R} = \text{Me}, \text{C}_6\text{H}_3\text{Me}_2-2,6$ ) have three or four  $\nu(\text{CO})$  and one ( $\text{R} = \text{Me}$ ) or two ( $\text{R} = \text{C}_6\text{H}_3\text{Me}_2-2,6$ )  $\nu(\text{NC})$  absorptions. An X-ray crystal structure of  $[\text{Re}_2(\text{CO})_6(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_4]$  does, however, confirm the expected staggered tetra-*cis*-equatorial geometry<sup>12</sup> (Figure 2h).

From the above discussion it is apparent that the num-

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Table VI. Selected Mass Spectral Fragments of  $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$ 

$m/z$	I <sup>a,b</sup>	II <sup>c,d</sup>	fragment
138	100	67	$\text{Mn}_2(\text{CO})^+$ , $\text{Mn}(\text{CNBu-}t)^+$
193	54	3	$\text{Mn}(\text{CNBu-}t)^+$
250	76	3	$\text{Mn}_2(\text{CO})_5^+$ , $\text{Mn}(\text{CO})_4(\text{CNBu-}t)^+$
277	76	16	$\text{Mn}_2(\text{CO})_3(\text{CNBu-}t)^+$ , $\text{Mn}(\text{CO})_2(\text{CNBu-}t)_2^+$
305	25	100	$\text{Mn}_2(\text{CO})_4(\text{CNBu-}t)^+$ , $\text{Mn}(\text{CO})_3(\text{CNBu-}t)_2^+$
332	<1	35	$\text{Mn}_2(\text{CO})_2(\text{CNBu-}t)_2^+$
360	<1	13	$\text{Mn}_2(\text{CO})_3(\text{CNBu-}t)_2^+$

<sup>a</sup> Polycrystalline sample of  $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$  containing both the 1,1 (20%) and 1,2 isomers (80%). <sup>b</sup> All intensities relative to  $m/z$  138 (100%). <sup>c</sup> Data recorded on 1,1- $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$ . <sup>d</sup> All intensities relative to  $m/z$  138 (67%).

ber of  $\nu(\text{CO})$  bands observed in an IR spectrum of a metal carbonyl complex of the type  $[\text{M}_2(\text{CO})_{10-n}\text{L}_n]$  ( $n = 1-4$ ) is often less than predicted by the application of group theory, due to possible band overlap. Further, group theory often predicts the same number of bands for alternate geometries. Hence the data above are not sufficient for an unambiguous assignment of substitution geometry, and this problem will be compounded for substituted metal trimers, tetramers, etc. However, used in conjunction with X-ray crystallography of selected complexes it is possible to establish a correlation between IR spectral data (absorption positions, intensity patterns) and substitution geometry. This correlation has been extended successfully to other geometries when L = phosphines, olefins, etc.<sup>30</sup>

**<sup>1</sup>H NMR Spectra.** The <sup>1</sup>H NMR spectra of the  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  ( $n = 1-4$ ) complexes are given in Table V. The  $\text{CH}_x$  ( $x = 2, 3$ ) resonance occurs as a singlet for the mono-, di- (exception MeNC, see below), and tetra-substituted derivatives as expected. For the trisubstituted derivatives this signal occurs as two resonances in a 2:1 ratio,<sup>10</sup> consistent with isomer Figure 2g which has been observed by X-ray crystallography.<sup>12</sup>

The NMR spectra show a trend of the  $\text{CH}_x$  ( $x = 2, 3$ ) resonances to lower field with increasing  $n$ . This trend to lower field is expected (consequence of increased electron density on the metal),<sup>11</sup> but the remarkable feature is in the linear shift with similar slopes for all the isocyanides studied. This provides strong evidence for the dimer being treated as a single unit and not as two poorly interacting halves.

In the case of the disubstituted derivative  $[\text{Re}_2(\text{CO})_8(\text{CNMe})_2]$ , the Me resonance occurs as two signals in a ratio of 1:5. This phenomenon has been observed previously for the  $\text{CH}_x$  ( $x = 2, 3$ ) resonance of a variety of  $[\text{Mn}_2(\text{CO})_8(\text{CNR})_2]$  complexes<sup>10</sup> and has been related to the presence of two disubstituted isomers in solution (Figure 2e or f).

**Mass Spectrometry.** Although mass spectrometry can be used to ascertain complex stoichiometry of the  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  derivatives, only in certain instances can it reveal information about product geometry. For instance the mass spectrum of  $[\text{Re}_2(\text{CO})_9(\text{CNBu-}t)]$  is consistent with the product stoichiometry (see supplementary material for fragments) but provides no information as to whether the RNC group is in the axial or equatorial position on the dimer. This also holds true for the higher substituted derivatives ( $n = 2-4$ ). However, the mass spectral data can give information as to whether the isonitrile ligands have a 1,1 or 1,2 arrangement with respect

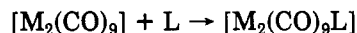
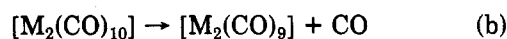
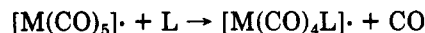
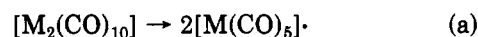
to the metal. This is indicated by data available on the related Mn derivatives  $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$ . (The Re disubstituted isomers, excluding  $[\text{Re}_2(\text{CO})_8(\text{CNMe})_2]$ , have only been observed with 1,2 geometry). Selected fragments of 1,1- and 1,2- $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$  (the spectra were run on a ~5:1 ratio of the 1,2 to 1,1 isomers) together with their relative intensities are given in Table VI (full data given in the supplementary material). The most dramatic relative intensity changes relate to the peaks  $m/z$  250 and 305. The  $m/z$  250 peak (1,2 isomer = 76%; 1,1 isomer = 3%) corresponds to the  $[\text{Mn}(\text{CO})_4(\text{CNBu-}t)]^+$  ion, and the intensity ratios are consistent with the isomer formulation. The difference in intensity of fragments lower down in the fragmentation scheme are less pronounced. Similarly the intensity of the peak  $m/z$  305 (1,2 isomer = 25%; 1,1 isomer = 100%), assigned to  $[\text{Mn}(\text{CO})_3(\text{CNBu-}t)_2]^+$ , is consistent with the proposed isomer geometries.

Application of the above patterns to the mass spectrum of  $[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_2]$ , for which an X-ray crystal structure determination has been obtained<sup>12</sup> is consistent with the data established above.

In this case, monomeric Re fragments are readily detected as Re has two isotopes, <sup>185</sup>Re (37.5%) and <sup>187</sup>Re (62.5%), and intense peaks corresponding to the fragments  $[\text{Re}_2(\text{CO})_{4-n}(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]^+$  are readily detected (see supplementary material). Further, no peaks corresponding to  $[\text{Re}(\text{CO})_{3-n}(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_2]^+$  ( $n = 0-3$ ) are observed. It is thus apparent that mass spectrometry provides a useful tool for establishing some features of isomer geometry.

**Mechanistic Studies.** The reaction between  $[\text{M}_2(\text{CO})_{10}]$  ( $\text{M}_2 = \text{Mn}_2, \text{Re}_2, \text{MnRe}$ ) and group 5 donor ligands has been extensively investigated and reviewed.<sup>7,8</sup> The kinetic data are consistent with two possible mechanisms outlined in Scheme I.<sup>7,8</sup> When  $\text{M}_2 = \text{Re}_2$  and L =  $\text{PPh}_3$ , labeling studies using <sup>185</sup>Re and <sup>187</sup>Re have clearly established that the simple CO dissociative pathway is operating (Scheme Ib).<sup>31</sup> The limited availability of the Re isotopes precludes extensive studies using these isotopes, but the problem can be overcome by using <sup>13</sup>CO as a label, as has been described for the  $[\text{Mn}_2(\text{CO})_{10}]$  system.<sup>9c</sup>

#### Scheme I



An investigation of the mechanism of the reaction between  $[\text{Re}_2(\text{CO})_{10}]$  and *t*-BuNC in the presence of PdO as catalyst, using <sup>13</sup>CO labeling procedures to determine whether the reaction occurred with or without metal-metal bond cleavage (cf. Scheme I) was undertaken. Reaction of an equimolar mixture  $[\text{Re}_2(^{12}\text{CO})_{10}]$  and  $[\text{Re}_2(^{13}\text{CO})_{10}]$  (synthesized from  $[\text{Re}_2(\text{CO})_{10}]$  and <sup>13</sup>CO) with *t*-BuNC in the presence of catalyst yielded  $[\text{Re}_2(^{12}\text{CO})_9(\text{CNBu-}t)]$  and  $[\text{Re}_2(^{13}\text{CO})_9(\text{CNBu-}t)]$  with negligible amount of CO scrambling. (The products were readily characterized by mass spectrometry.) The data clearly indicate that the

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dominant if not exclusive reaction occurs with no Re-Re bond cleavage and is consistent with similar results obtained for the reaction between  $[\text{Mn}_2(\text{CO})_{10}]$  and *t*-BuNC in the presence of Pd/C as catalyst<sup>9c</sup> and hence rules out the radical substitution process (Scheme Ia) for the catalyzed reaction. The results do not however indicate whether the catalyzed reaction occurs via an associative process or dissociate process similar to the uncatalyzed reaction, and further kinetic investigations will be needed to establish this feature of the mechanism.

Reaction of  $[\text{Re}_2(\text{CO})_{10}]$  and 2 equiv of *t*-BuNC in the presence of Pd/CaCO<sub>3</sub> leads exclusively to 1,2-*dieq*- $[\text{Re}_2(\text{CO})_8(\text{CNBu-}t)_2]$ . Attempts to isomerize this complex to the 1,1 isomer (125 °C, 6 h) in both the presence and absence of catalyst failed.<sup>29</sup> The 1,1 isomer, independently synthesized from  $\text{Na}[\text{Re}(\text{CO})_5]$  and  $\text{Re}(\text{CO})_3(\text{CNBu-}t)_2\text{I}$ , also failed to isomerize to the 1,2 isomer in both the presence and absence of the Pd/CaCO<sub>3</sub> catalyst. The 1,2 isomer is thus the kinetic product of the catalyzed reaction. This product could, however, arise from the loss of the two CO groups either from the same<sup>9a</sup> or different Re atoms and would depend on the cis-labilizing effects<sup>33</sup> of the ligands and metal carbonyl fragments.

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**Registry No.**  $[\text{Re}_2(\text{CO})_9(\text{CNBu-}t)]$ , 79138-90-2; 1,2- $[\text{Re}_2(\text{CO})_8(\text{CNBu-}t)_2]$ , 95672-44-9; 1,1- $[\text{Re}_2(\text{CO})_8(\text{CNBu-}t)_2]$ , 95590-05-9;  $[\text{Re}_2(\text{CO})_7(\text{CNBu-}t)_3]$ , 95590-06-0;  $[\text{Re}_2(\text{CO})_9(\text{CNCH}_2\text{C}_6\text{H}_5)]$ , 95590-07-1;  $[\text{Re}_2(\text{CO})_9(\text{CNCH}_2\text{C}_6\text{H}_5)_2]$ , 95590-08-2;  $[\text{Re}_2(\text{CO})_9(\text{CNCH}_2\text{C}_6\text{H}_5)_3]$ , 95590-09-3;  $[\text{Re}_2(\text{CO})_9(\text{CNC}_6\text{H}_{11})]$ , 95590-10-6;  $[\text{Re}_2(\text{CO})_9(\text{CNC}_6\text{H}_{11})_2]$ , 95590-11-7;  $[\text{Re}_2(\text{CO})_7(\text{CNC}_6\text{H}_{11})_3]$ , 95590-12-8;  $[\text{Re}_2(\text{CO})_9(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$ , 95590-13-9;  $[\text{Re}_2(\text{CO})_9(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_2]$ , 95406-94-3;  $[\text{Re}_2(\text{CO})_7(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_3]$ , 95590-14-0;  $[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_4]$ , 95590-15-1;  $[\text{Re}_2(\text{CO})_9(\text{CNMe})]$ , 95672-45-0; 1,1- $[\text{Re}_2(\text{CO})_8(\text{CNMe})_2]$ , 95590-16-2; 1,2- $[\text{Re}_2(\text{CO})_8(\text{CNMe})_2]$ , 95590-17-3;  $[\text{Re}_2(\text{CO})_7(\text{CNMe})_3]$ , 95406-95-4;  $[\text{Re}_2(\text{CO})_8(\text{CNMe})_4]$ , 95590-18-4;  $[\text{Re}_2(^{13}\text{C})_9(\text{CNBu-}t)]$ , 95590-19-5;  $[\text{Re}_2(\text{CO})_{10}]$ , 14285-68-8;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ , 38117-54-3; 1,1- $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$ , 94901-45-8; 1,2- $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$ , 95672-46-1;  $[\text{Re}_2(^{13}\text{C})_{10}]$ , 95590-20-8;  $\text{Na}[\text{Re}(\text{CO})_5(\text{CNBu-}t)_2]$ , 95590-21-9;  $[\text{Re}(\text{CO})_5\text{I}]$ , 13821-00-6;  $[\text{Re}_2(\text{CO})_8(\text{CNBu-}t)(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$ , 95590-22-0; PdO, 1314-08-5; CaCO<sub>3</sub>, 471-34-1; BaCO<sub>3</sub>, 513-77-9; BaSO<sub>4</sub>, 7727-43-7; Al<sub>2</sub>O<sub>3</sub>, 1344-28-1; CoCl<sub>2</sub>, 7646-79-9; IrCl<sub>3</sub>, 10025-83-9; K<sub>2</sub>PtCl<sub>4</sub>, 10025-99-7; PtBr<sub>2</sub>, 13455-12-4; PtO<sub>2</sub>, 1314-15-4; LiAlH<sub>4</sub>, 16853-85-3; *t*-BuNC, 7188-38-7; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NC, 10340-91-7; C<sub>6</sub>H<sub>11</sub>NC, 931-53-3; 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, 2769-71-3; MeNC, 593-75-9; Pd, 7440-05-3; Pt, 7440-06-4; Zn, 7440-66-6; Rh, 7440-16-6; Ru, 7440-18-8; Re, 7440-15-5; C, 7440-44-0.

**Supplementary Material Available:** Tables of mass spectra data for  $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$  and 1,2- $[\text{Re}_2(\text{CO})_8(\text{CNBu-}t)_2]$  (3 pages). Ordering information is given on any current masthead page.

## Systematic Substitution of $[\text{Re}_2(\text{CO})_{10}]$ . The Crystal and Molecular Structure of a Series of $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$ Complexes ( $n = 1, R = t\text{-Bu}$ ; $n = 2, 4, R = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ; $n = 3, R = \text{Me}$ )

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The crystal and molecular structures of a series of isocyanide derivatives of  $\text{Re}_2(\text{CO})_{10}$  have been determined.  $[\text{Re}_2(\text{CO})_8(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_2]$ : space group  $P\bar{1}$ ,  $Z = 2$ ,  $a = 15.145$  (7) Å,  $b = 9.294$  (4) Å,  $c = 10.328$  (4) Å,  $\alpha = 92.70$  (3)°,  $\beta = 74.47$  (2)°,  $\gamma = 98.85$  (3)°.  $[\text{Re}_2(\text{CO})_7(\text{CNMe})_3]$ :  $P2_1/n$ ,  $Z = 4$ ,  $a = 10.874$  (5) Å,  $b = 16.175$  (7) Å,  $c = 10.711$  (5) Å,  $\beta = 90.07$  (3)°.  $[\text{Re}_2(\text{CO})_6(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_4]$ :  $Pccn$ ,  $Z = 4$ ,  $a = 13.832$  (6) Å,  $b = 11.322$  (5) Å,  $c = 26.401$  (11) Å. The structures were refined to  $R$  values of 0.039, 0.060, and 0.110, respectively. A redetermination of the structure of  $[\text{Re}_2(\text{CO})_9(\text{CN-}t\text{-Bu})]$  to include absorption corrections yielded an  $R$  value of 0.051. In all four structures, the ligand conformation was found to be staggered when viewed down the Re-Re bond with the isocyanide ligands occupying cis-equatorial positions. An increase in the Re-Re bond length in  $[\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n]$  ( $n = 1-4$ ) with increasing degree of isocyanide substitution was only observed when  $n = 4$ , and this could be ascribed to steric rather than electronic factors.

### Introduction

$[\text{Re}_2(\text{CO})_{10}]$  and  $[\text{Mn}_2(\text{CO})_{10}]$  are examples of metal dimers, and their ready availability and moderate air stability have resulted in extensive studies of their chemical and physical properties.<sup>1</sup> Both compounds have been

characterized by single-crystal X-ray diffraction techniques,<sup>2-4</sup> and in both instances the structures contain a single long metal-metal bond, no bridging carbonyls, and

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