

# Mixed-Metal Dimers. 3.<sup>†</sup> Substitution Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{M}(\text{CO})_5]$ (M = Mn, Re) and the X-ray Crystal Structure Determination of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{M}(\text{CO})_4(\text{CNBu-}t)]$ (M = Mn, Re)

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The reaction between  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{M}(\text{CO})_5]$  (M = Mn, 1; M = Re, 2) and L (L = *t*-BuNC, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, PMePh<sub>2</sub>, P(OMe)<sub>3</sub>) under a variety of conditions is reported. Reaction between 2 and L (either thermally at 90 °C, or in the presence of PdO as catalyst, or Me<sub>3</sub>NO) gives only the Re-substituted product  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4\text{L}]$ . All attempts to synthesize the Fe-substituted complex, e.g., via the reaction between  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNR})]^+$  and  $[\text{Re}(\text{CO})_5]^-$ , failed. The thermal reaction between 1 and L yielded the Fe-substituted salts  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{L}_2]^+$  or  $[(\eta^5\text{-C}_5\text{H}_5)\text{FeL}_3]^+$ . However, reaction of 1 with Me<sub>3</sub>NO followed by addition of L yielded either  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{CNR})]$  (R = *t*-Bu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC) or  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{L}_2]$  and  $[\text{Mn}_2(\text{CO})_8\text{L}_2]$  (L = P(OMe)<sub>3</sub>, PMePh<sub>2</sub>). Attempts to synthesize the Fe-substituted mixed-metal dimers failed. The new substituted mixed-metal dimers were completely characterized by IR, NMR, and mass spectrometry as well as thermal and photochemical decomposition studies. The crystal and molecular structures of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{M}(\text{CO})_4(\text{CNBu-}t)]$  (M = Mn, 3; M = Re, 4) were determined. 3: space group *P*2<sub>1</sub>/*c*, *Z* = 4, *a* = 8.715 (2) Å, *b* = 13.884 (2) Å, *c* = 15.579 (3) Å, β = 96.95 (2)°. 4: space group *P*2<sub>1</sub>/*n*, *a* = 11.313 (2) Å, *b* = 11.055 (4) Å, *c* = 15.732 (3) Å, β = 107.03 (1)°. The structures were refined to *R* values of 0.050 and 0.037, respectively. In both structures the *t*-BuNC was attached to the non-Fe atom and in an equatorial site.

## Introduction

The search for rational routes to the synthesis of low oxidation state complexes containing more than one metal center is a dominant theme in the field of dimer and cluster<sup>1-3</sup> chemistry. In more recent years, the exploration of the chemistry of these complexes, methodology to stabilize dimers and clusters,<sup>4</sup> the addition and removal of metal centres to clusters,<sup>5</sup> and studies on metal core rearrangement processes<sup>6</sup> have also been reported. However, to date, very few systematic studies on the relationship between the chemistry of monometallic fragments and corresponding dimer or cluster complexes have appeared in the literature. The relationship between the reactivity of fragments and the corresponding cluster molecules need not be straightforward, and unexpected reaction pathways or products may be observed. This is exemplified by the CO substitution chemistry of, for example,  $[\text{M}_4(\text{CO})_{12}]$  (M = Ir,<sup>7a</sup> Co<sup>7b</sup>),  $[\text{MnRe}(\text{CO})_{10}]$ ,<sup>8,9</sup> and  $[\text{CoRu}(\text{CO})_7(\mu\text{-PPh}_2)]$ <sup>10</sup> in which metal-metal cooperative effects are proposed to occur. Thus an exploration of the factors that influence reactivity patterns and in particular factors that influence the site selectivity of reagent attack in metal dimer<sup>9-11</sup> and cluster complexes<sup>12</sup> is still needed.

Our own interest in the above site selectivity problem arose from our use of catalysts in the CO substitution reactions of transition-metal dimer complexes.<sup>13</sup> The use of catalysts enables the substitution reactions to occur under mild conditions and consequently in preference to potential competitive metal-metal bond cleavage reactions. In particular the investigation of the substitution reaction of  $[\text{MnRe}(\text{CO})_{10}]$  by isocyanides, RNC, revealed that the major isolated mono- and disubstituted products were the Re- and not the Mn-substituted complexes<sup>9</sup> which had been anticipated from our earlier studies on related Mn and Re carbonyl systems.<sup>14</sup> Consequently we have embarked on a program to investigate this site selectivity phenomenon in a range of cluster and dimer complexes

and in particular to ascertain whether reactivity can be induced at specific metal centers in multimetallic systems by rational procedures.

Our approach to this aspect of the chemistry of multimetallic complexes has involved a study (initially) of systems involving only one metal-metal bond and in particular the substitution reactions of heteronuclear transition-metal carbonyl dimer complexes. In this pub-

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<sup>†</sup> For part 1, see ref 9 and for part 2, ref 15.

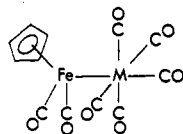


Figure 1. Structure of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{M}(\text{CO})_5]$  ( $\text{M} = \text{Mn, Re}$ ).

lication we report on the reactions of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{M}(\text{CO})_5]$  (Figure 1;  $\text{M} = \text{Mn}$ , 1;  $\text{M} = \text{Re}$ , 2) with  $t\text{-BuNC}$ ,  $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$ ,  $\text{PMePh}_2$ , or  $\text{P}(\text{OMe})_3$ . Also reported are the crystal structure determinations of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{M}(\text{CO})_4(\text{CNBu-t})]$  ( $\text{M} = \text{Mn, Re}$ ). A preliminary report of some aspects of this work has been published.<sup>15</sup>

### Experimental Section

$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ,  $[\text{Mn}_2(\text{CO})_{10}]$ , and  $[\text{Re}_2(\text{CO})_{10}]$  were purchased from Strem Chemicals, and the PdO catalyst was purchased from Johnson-Matthey Chemicals.  $\text{Me}_3\text{NO}$  was purchased from Aldrich Co. Ltd. and where indicated was dried by using a Dean-Stark apparatus (toluene as solvent).  $[\text{Mn}(\text{CO})_4(\text{CNBu-t})]_2$ ,<sup>16</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-t})\text{I}]$ ,<sup>17</sup> and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}]$ <sup>18a</sup> were synthesized by literature procedures. All the reactions were routinely carried out under nitrogen in degassed and distilled solvents. Reactions performed in the dark were carried out in foil wrapped flasks. Column chromatography was performed on silica gel (Merck 60F, 70–230 mesh). Preparative TLC was performed on  $20 \times 20$  cm alumina plates of 250- $\mu\text{m}$  thickness (Merck Chemicals).

Infrared spectra were recorded on either a Pye Unicam SP 300 or Jasco IRA-1 spectrophotometer, NMR spectra on a Bruker WP80 FT NMR spectrometer, and mass spectra on either a Finnegan Mat 8200 or an AEI MS9 spectrometer. Melting points were recorded on a Kofler micro hot-stage apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratories, CSIR, Pretoria. Photochemical decomposition reactions were performed by using a low-pressure Hanovia 100-W lamp.

**Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5]$  (1) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_5]$  (2).**  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}]$  (20 mmol) was added to a solution of  $\text{Na}[\text{M}(\text{CO})_5]$ <sup>18b</sup> prepared from  $[\text{M}_2(\text{CO})_{10}]$  ( $\text{M} = \text{Mn, Re}$ ; 10 mmol) and  $\text{Na}/\text{Hg}$  (600 mg of  $\text{Na}/5$  mL of  $\text{Hg}$ ) in THF (60 mL). Reaction progress was monitored by IR spectroscopy, and the reaction was considered complete after stirring for 2 days in the dark. Methanol (10 mL) was then added to the mixture, and the solution was pumped to dryness. The residue was taken up in benzene and centrifuged, and the supernatant liquid was removed, concentrated, and subjected to column chromatography (silica, eluent hexane). The required mixed-metal dimer was isolated from a bright red band, 1, or dark yellow band, 2, eluted from the column (50% yield). Spectroscopic data for the dimers are given in Table I.

**Direct Reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5]$  with L** ( $\text{L} = t\text{-BuNC}$ ,  $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$ ,  $\text{PMePh}_2$ ,  $\text{P}(\text{OMe})_3$ ).  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5]$  (0.54 mmol) in THF (15 mL) was reacted in the dark with the required number of equivalents of L such that all the starting material was consumed (see Table II), as indicated by solution infrared spectra. Upon completion of the reaction,  $\text{NH}_4\text{PF}_6$  (0.55 mmol) was added to the reaction mixture that was then pumped to dryness. The residue was washed with benzene ( $2 \times 15$  mL) and with hexane (15 mL) to remove the non-salt products. The salt products were recrystallized from dichloromethane–ether–hexane to yield yellow crystalline products (Table

Table I. Spectroscopic Data for the Carbonyl Complexes Described in This Work

complex	IR <sup>a,b</sup> /cm <sup>-1</sup>			NMR <sup>c</sup> / $\delta$			mass spectrum, <sup>d</sup> $m/z$
	PNC	$\nu_{\text{CO}}$	other	C <sub>5</sub> H <sub>5</sub>	Me	other	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5]$		2088 (m)	2018 (m)	1990 (m)	1976 (s)	1945 (w)	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{CNBu-t})]$	2153 (m)	2034 (m)	1971 (vs)	1955 (sh)	1945 (s)	1920 (w)	427
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})]$	2128 (m)	2031 (m)	1976 (vs)	1959 (sh)	1950 (s)	1925 (w)	475
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-t})_2][\text{PF}_6]$	2187 (s)	2166 (s)	2021 (s)				
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-t})_2][\text{PF}_6]$	2160 (m)	2115 (s)					
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PMePh}_2)_2][\text{PF}_6]$		1968 (s)					
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{P}(\text{OMe})_3)_2][\text{PF}_6]$		1993 (s)					
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CNBu-t})][\text{BF}_4]$	2196 (m)	2077 (s)	2041 (s)				
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})][\text{BF}_4]$	2178 (m)	2077 (s)	2041 (s)				
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_5]$		2099 (m)	2021 (w)	1993 (vs)	1975 (s)	1933 (m)	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{CNBu-t})]$	2182 (m)	2068 (m)	2000 (sh)	1982 (vs)	1951 (sh)	1910 (m)	559
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})]$	2155 (m)	2062 (m)	1999 (sh)	1984 (vs)	1954 (sh)	1915 (m)	607
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{PMePh}_2)]$		2061 (m)	2018 (w)	1985 (sh)	1962 (vs)	1933 (s)	676
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{P}(\text{OMe})_3)]$		2070 (w)	1996 (m)	1986 (m)	1968 (vs)	1934 (m)	600

<sup>a</sup> Recorded in hexane or dichloromethane (salts). <sup>b</sup> Abbreviations: sh, shoulder; w, weak; m, medium; s, strong; vs, very strong. <sup>c</sup> Recorded in C<sub>6</sub>D<sub>6</sub> or CDCl<sub>3</sub> (salts) relative to Me<sub>4</sub>Si; d, doublet. <sup>d</sup> Parent ion. <sup>e</sup> Virtual triplet. <sup>f</sup>  $J = 10.9$  Hz. <sup>g</sup>  $J = 8.3$  Hz. <sup>h</sup>  $J = 12.2$  Hz.

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**Table II. Reaction Conditions and Product Yields for the Direct Reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5]$  and L**

ligand	equiv added <sup>a</sup>	reactn time, <sup>b</sup> min	product	yield, <sup>c</sup> %
<i>t</i> -BuNC <sup>d</sup>	2	10	$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)_2][\text{PF}_6]$	70
2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC <sup>e</sup>	3	4	$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)_3][\text{PF}_6]$	90
PMePh <sub>2</sub>	2	20	$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PMePh}_2)_2][\text{PF}_6]$	90
P(OMe) <sub>3</sub>	2	15	$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{P}(\text{OMe})_3)_2][\text{PF}_6]$	80

<sup>a</sup> Addition of indicated equivalents resulted in disappearance of starting material as detected by IR spectroscopy. <sup>b</sup> Room-temperature reaction; time until disappearance of starting material as detected by IR spectroscopy. <sup>c</sup> After recrystallization and isolation as the PF<sub>6</sub> salt. <sup>d</sup> Anal. Calcd for C<sub>16</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub>FeP: C, 41.6; H, 5.03; N, 6.04. Found: C, 41.1; H, 5.09; N, 6.26. <sup>e</sup> Anal. Calcd for C<sub>32</sub>H<sub>32</sub>N<sub>3</sub>F<sub>6</sub>FeP: C, 58.3; H, 4.89; N, 6.37. Found: C, 59.0; H, 4.71; N, 6.38.

II). Spectroscopic data for these products are given in Table I.

**The Me<sub>3</sub>NO-Induced Reaction between  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5]$  and L (L = *t*-BuNC, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, P(OMe)<sub>3</sub>, PMePh<sub>2</sub>).** Dropwise addition of Me<sub>3</sub>NO (0.65 mmol) in CH<sub>3</sub>CN (15 mL) to a solution of 1 (0.54 mmol) in CH<sub>3</sub>CN (8 mL) in the dark resulted in the disappearance of starting material and formation of a new complex [IR (CH<sub>3</sub>CN) 2034 (m), 1958 (vs), 1918 (s) cm<sup>-1</sup>]. L (0.6 mmol) was added to this solution, and further changes in the IR spectrum were observed. The solution was pumped to dryness, and the components were separated by preparative TLC (alumina, eluent hexane). When L = P(OMe)<sub>3</sub> or PMePh<sub>2</sub>, major yellow and red bands were removed from the TLC plate and after extraction were identified by their NMR and IR spectra as  $[\text{Mn}(\text{CO})_4\text{L}]_2^{21}$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ , respectively (total yield 55%). When L = RNC, a red band was removed from the TLC plate and after extraction and recrystallization from pentane gave the required products as dark red crystals in approximately 40% yield.  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{CNBu-}t)]$ : mp 63 °C. Anal. Calcd for C<sub>16</sub>H<sub>14</sub>NO<sub>6</sub>FeMn: C, 45.0; H, 3.3; N, 3.28. Found: C, 44.6; H, 3.1; N, 3.27.  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)]$ : mp 89 °C. Anal. Calcd for C<sub>20</sub>H<sub>14</sub>NO<sub>6</sub>FeMn: C, 50.6; H, 3.0; N, 3.0. Found: C, 50.5; H, 2.8; N, 2.9. Spectroscopic data for the substituted dimers are shown in Table I.

**Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CNR})][\text{BF}_4]$  (R = *t*-Bu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).**  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$  (2.5 mmol) and AgBF<sub>4</sub> (3.1 mmol) were reacted in dichloromethane (15 mL) for 30 min. Formation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_2\text{Cl}_2)][\text{BF}_4]^{21}$  was monitored by solution infrared spectroscopy [IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>CO</sub> 2065 (s), 2022 (s) cm<sup>-1</sup>]. The solution was centrifuged, and the supernatant liquid was transferred by syringe to a nitrogen-filled round-bottomed flask. RNC (2.6 mmol) was added, and upon completion of the reaction (monitored by IR spectroscopy) the solvent was removed in vacuo. The residue was washed repeatedly with benzene and recrystallized from dichloromethane-ether. The tan crystals were further washed with ether and benzene and then dried in vacuo. Spectroscopic data for the new complexes are given in Table I.

**The Reactions of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_5]$  with RNC (R = *t*-Bu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).** (a) **PdO-Catalyzed Reaction.** RNC (0.42 mmol) was added to a solution of 2 (0.42 mmol) in THF (15 mL) at room temperature in the dark. PdO catalyst (10 mg) was then added to the solution, and the reaction, monitored by IR spectroscopy, indicated rapid reactant disappearance (R = *t*-Bu, 25 min; R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 15 min). After solvent removal in vacuo, the products were crystallized from toluene-hexane to give pure yellow-brown crystals in quantitative yield.  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{CNBu-}t)]$ : mp 54 °C. Anal. Calcd for C<sub>16</sub>H<sub>14</sub>NO<sub>6</sub>FeRe: C, 34.4; H, 2.5; N, 2.5. Found: C, 34.0; H, 2.3; N, 2.5.  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)]$ : mp 106 °C. Anal. Calcd for C<sub>20</sub>H<sub>14</sub>NO<sub>6</sub>FeRe: C, 39.6; H, 2.3; N, 2.5. Found: C, 39.7; H, 2.1; N, 2.3. Spectroscopic data for the new dimer complexes are shown in Table I.

(b) **Me<sub>3</sub>NO Route.** Dry Me<sub>3</sub>NO (0.54 mmol) was added to a solution of 2 (0.42 mmol) in CH<sub>3</sub>CN (15 mL) at room temperature in the dark. Monitoring the reaction by IR spectroscopy indicated rapid (5-min) formation of a new complex [IR (CH<sub>3</sub>CN) ν<sub>CO</sub> 2060 (m), 1979 (s), 1943 (w), 1915 (m), 1891 (w) cm<sup>-1</sup>]. *t*-BuNC (0.42 mmol) was added to the solution, and after completion of the reaction, as determined by IR spectroscopy, the solvent was

removed in vacuo. The residue was purified by column chromatography (silica, eluent hexane (100 mL) followed by benzene-hexane, 50/50 v/v) and yielded pure  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{CNBu-}t)]$  in 60% yield. Spectroscopic product characterization was identical with that of the PdO-catalyzed reaction, (a) above.

(c) **Thermal Reaction.** Dimer 2 (0.42 mmol) was reacted with *t*-BuNC (0.42 mmol) in dioxane (20 mL) at 85 °C in the dark. The reaction was monitored by IR spectroscopy and indicated that the reaction proceeded rapidly (15 min) to give a quantitative yield of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{CNBu-}t)]$ . After cooling, the reaction solvent was removed in vacuo and the product was crystallized from toluene-hexane. Spectroscopic product characterization was identical with that of the PdO-catalyzed reaction (a) above.

**Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{L})]$  (L = PMePh<sub>2</sub>, P(OMe)<sub>3</sub>).** Dimer 2 (0.42 mmol) and L (0.85 mmol) were reacted in refluxing toluene (15 mL) in the dark. The reaction proceeded slowly over several hours (L = P(OMe)<sub>3</sub>, 4 h; L = PMePh<sub>2</sub>, 8 h). Upon consumption of the starting materials, the reaction mixture was cooled and the solvent was removed in vacuo. The reaction products were purified by preparative TLC (alumina, eluent hexane/benzene, 85/15 v/v) to give pure  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{L})]$ .  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{PMePh}_2)]$ : mp 102 °C. Anal. Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>6</sub>PF<sub>6</sub>Re: C, 42.68; H, 2.69. Found: C, 42.92; H, 2.42. Spectroscopic data for the new complexes are found in Table I.

**Attempted Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)\text{M}(\text{CO})_5]$  (M = Mn, Re).**  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)]\text{BF}_4$  was prepared by the room-temperature reaction between  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)]$  (0.42 mmol) and AgBF<sub>4</sub> (0.49 mmol) in THF (15 mL). After 1 h the solution was centrifuged and the supernatant liquid was transferred by using cannula tubing into a nitrogen-filled flask. Na[M(CO)<sub>5</sub>], prepared from [M<sub>2</sub>(CO)<sub>10</sub>] (M = Mn, Re; 0.22 mmol) and excess Na/Hg (80 mg of Na; 5 mL of Hg) in THF (15 mL), was added dropwise via cannula tubing to the above solution. The reaction was monitored by IR spectroscopy and was determined to be over in 15 min, at which time solvent was removed in vacuo. The non-salt products were extracted with benzene and analyzed by IR and NMR spectroscopy. The spectra could be completely analyzed and did not indicate the presence of a complex corresponding to the required product (see discussion).

**X-ray Crystal Structure Analysis of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{M}(\text{CO})_4(\text{CNBu-}t)]$  (M = Mn, 3; M = Re, 4).** Crystals of 3 (obtained from the indirect reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5]$  with NMe<sub>3</sub>O and *t*-BuNC) and crystals of 4 (from the PdO-catalyzed reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_5]$  with *t*-BuNC) were grown from pentane and a solution of toluene-hexane, respectively, under nitrogen at -20 °C.

A single crystal of 3 was mounted in a Lindemann tube and that of 4 was mounted on a glass fiber. Lattice constants were measured and refined from 25 reflections in the range 16 < θ < 19° on an automatic Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. The crystal data and crystallographic details appear in Table III. Intensity data were collected for both crystals on the diffractometer within the ranges 3 ≤ θ ≤ 27° and 3 ≤ θ ≤ 30° for 3 and 4, respectively. Standard reflections were measured every hour of exposure time. There was no indication of decay during the two data collections. The data were corrected for Lorentz-polarization effects, and an empirical absorption correction<sup>22</sup> was applied to each set of data.

**Table III. Crystal Data and Details of the Structure Analysis for the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{M}(\text{CO})_4(\text{CNBu-}t)]$  (M = Mn, Re) Complexes**

	3	4
complex	$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{CNBu-}t)]$	$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{CNBu-}t)]$
formula	$\text{FeMnC}_{16}\text{H}_{14}\text{NO}_6$	$\text{FeReC}_{16}\text{H}_{14}\text{NO}_6$
$M_r$	427.07	558.34
color, shape	dark red plates	yellow-brown plates
space group	$P2_1/c$	$P2_1/n$
$a$ , Å	8.715 (2)	11.313 (2)
$b$ , Å	13.884 (2)	11.055 (4)
$c$ , Å	15.579 (3)	15.732 (3)
$\beta$ , deg	96.95 (2)	107.03 (1)
$U$ , Å <sup>3</sup>	1871.19	1881.25
$Z$	4	4
$F(000)$	864	1064
$D(\text{calcd})$ , g cm <sup>-3</sup>	1.52	1.97
$\mu$ , cm <sup>-1</sup>	14.02	69.20
$\lambda(\text{Mo K}\alpha)$ , Å	0.71069	0.71069
scan mode	$\omega/2\theta$	$\omega/2\theta$
range, deg	$3 \leq \theta \leq 27$	$3 \leq \theta \leq 30$
scan width, deg	$0.6 + 0.35 \tan \theta$	$0.6 + 0.35 \tan \theta$
variable scan speed, deg min <sup>-1</sup>	0.97–5.49	0.97–5.49
range of $hkl$	$\pm h, +k, +l$	$\pm h, +k, +l$
measd intensities	4512	5902
unique reflectns	3654	5008
internal consistency	0.040	0.023
$R$ index <sup>a</sup>	0.050	0.037
omitted reflectns	696	960
cutoff criterion	$F < 3\sigma(F)$	$F < 4\sigma(F)$
weighting scheme	unit wights	unit weights
no. of variables	258	227
max shift/esd (non-H)	0.61	0.08
max peak in diff map e Å <sup>-3</sup>	0.61	0.69

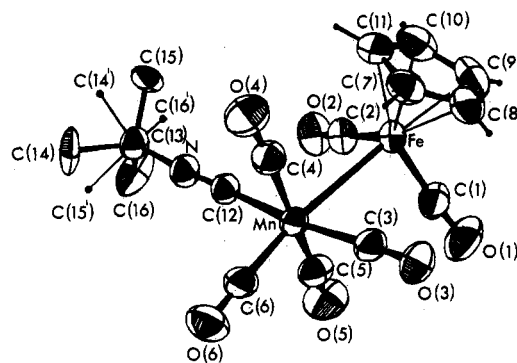
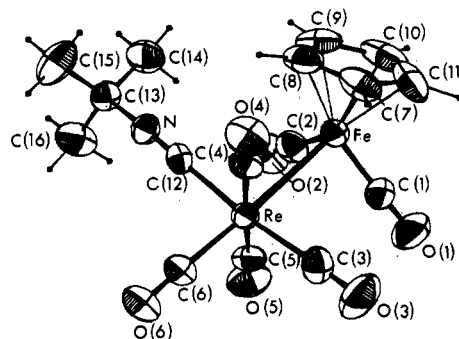
<sup>a</sup>The conventional  $R$  is defined by  $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ , where  $F_o$  is the observed structure factor and  $F_c$  the calculated structure factor.

**Table IV. Fractional Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Temperature Factors ( $\text{Å}^2, \times 10^3; \times 10^4$  for Mn and Fe) for Non-Hydrogen Atoms of 3**

	$x/a$	$y/b$	$z/c$	$U(\text{eq})$
Mn	684 (1)	114 (1)	3286 (1)	473 (4)
Fe	3138 (1)	1438 (1)	3173 (1)	522 (4)
N(1)	-1369 (5)	722 (4)	1650 (3)	60 (3)
O(1)	5241 (7)	-176 (5)	3117 (4)	105 (5)
O(2)	2116 (6)	1341 (4)	1338 (3)	79 (3)
O(3)	2872 (6)	-292 (4)	4857 (3)	76 (3)
O(4)	2156 (8)	-1295 (5)	2202 (4)	101 (4)
O(5)	-903 (7)	1740 (4)	4056 (4)	92 (4)
O(6)	-1516 (7)	-1320 (4)	3807 (4)	84 (3)
C(1)	4359 (8)	438 (6)	3141 (5)	74 (4)
C(2)	2459 (7)	1364 (5)	2070 (4)	61 (4)
C(3)	2067 (8)	-113 (5)	4253 (4)	61 (4)
C(4)	1625 (9)	-753 (5)	2626 (4)	66 (4)
C(5)	-231 (8)	1123 (5)	3784 (4)	63 (4)
C(6)	-677 (8)	-758 (5)	3589 (4)	61 (4)
C(7)	2711 (10)	2240 (5)	4301 (5)	69 (4)
C(8)	4264 (12)	2006 (7)	4325 (7)	77 (6)
C(9)	4848 (12)	2423 (8)	3621 (7)	84 (6)
C(10)	3681 (12)	2905 (7)	3131 (6)	82 (5)
C(11)	2354 (11)	2790 (5)	3546 (6)	73 (5)
C(12)	-574 (7)	503 (5)	2246 (4)	53 (3)
C(13)	-2408 (4)	1091 (3)	902 (2)	56 (3)
C(14)	-4039 (6)	956 (8)	1062 (5)	55 (7)
C(15)	-2096 (11)	2131 (5)	784 (6)	58 (7)
C(16)	-2122 (11)	553 (8)	113 (4)	70 (8)
C(14')	-3378 (13)	1878 (8)	1193 (5)	184 (4) <sup>a</sup>
C(15')	-3415 (13)	297 (6)	526 (7)	184 (4) <sup>a</sup>
C(16')	-1469 (8)	1466 (10)	241 (5)	184 (4) <sup>a</sup>

<sup>a</sup>Isotropic temperature factor.

The structures were solved by Patterson methods, and subsequent Fourier synthesis revealed the remaining non-hydrogen atoms. Refinement was carried out by means of full-matrix least-squares

**Figure 2. An ORTEP plot of the structure of 3.****Figure 3. An ORTEP plot of the structure of 4.**

calculations in which the hydrogen atoms were included at calculated positions. All non-hydrogen atoms were assigned anisotropic temperature factors, and  $R$  values converged to 0.0504 and 0.0369 for 3 and 4, respectively. Since most weak reflections were treated as unobserved, different weighting schemes had little effect on the refinement and unit weights were used for the final refinements.

The *tert*-butyl group in 3 showed considerable rotational disorder. Two rigid bodies were set up to coincide with the six

**Table V. Bond Lengths (Å) and Angles (deg) for Non-Hydrogen Atoms of 3**

Bond Lengths			
Mn-Fe	2.841 (1)	Mn-C(3)	1.839 (6)
Mn-C(4)	1.838 (7)	Mn-C(5)	1.831 (7)
Mn-C(6)	1.798 (7)	Mn-C(12)	1.920 (5)
Fe-C(1)	1.752 (7)	Fe-C(2)	1.752 (6)
Fe-C(7)	2.151 (7)	Fe-C(8)	2.094 (7)
Fe-C(9)	2.080 (7)	Fe-C(10)	2.095 (8)
Fe-C(11)	2.104 (7)	N(1)-C(12)	1.131 (6)
N(1)-C(13)	1.478 (3)	O(1)-C(1)	1.152 (8)
O(2)-C(2)	1.144 (6)	O(3)-C(3)	1.132 (6)
O(4)-C(4)	1.137 (7)	O(5)-C(5)	1.148 (7)
O(6)-C(6)	1.148 (7)	C(7)-C(8)	1.387 (11)
C(7)-C(11)	1.404 (10)	C(8)-C(9)	1.391 (12)
C(9)-C(10)	1.370 (12)	C(10)-C(11)	1.401 (11)
C(13)-C(14)	1.485 (3)	C(13)-C(15)	1.485 (3)
C(13)-C(16)	1.485 (3)	C(13)-C(14')	1.486 (3)
C(13)-C(15')	1.485 (3)	C(13)-C(16')	1.485 (3)
C(14)-C(14')	1.408 (11)	C(14)-C(15')	1.394 (11)
C(15)-C(14')	1.397 (11)	C(15)-C(16')	1.407 (11)
C(16)-C(15')	1.409 (11)	C(16)-C(16')	1.395 (11)

Bond Angles			
Fe-Mn-C(3)	74.8 (2)	Fe-Mn-C(4)	89.9 (2)
C(3)-Mn-C(4)	93.1 (3)	Fe-Mn-C(5)	84.3 (2)
C(3)-Mn-C(5)	93.4 (3)	C(4)-Mn-C(5)	169.9 (3)
Fe-Mn-C(6)	167.8 (2)	C(3)-Mn-C(6)	93.3 (3)
C(4)-Mn-C(6)	93.4 (3)	C(5)-Mn-C(6)	93.9 (3)
Fe-Mn-C(12)	97.1 (2)	C(3)-Mn-C(12)	171.8 (3)
C(4)-Mn-C(12)	87.8 (3)	C(5)-Mn-C(12)	84.8 (3)
C(6)-Mn-C(12)	94.8 (2)	Mn-Fe-C(1)	87.3 (2)
Mn-Fe-C(2)	81.7 (2)	C(1)-Fe-C(2)	93.5 (3)
Mn-Fe-C(7)	94.5 (2)	C(1)-Fe-C(7)	126.8 (3)
C(2)-Fe-C(7)	139.5 (3)	Mn-Fe-C(8)	118.0 (3)
C(1)-Fe-C(8)	95.7 (3)	C(2)-Fe-C(8)	158.6 (4)
C(7)-Fe-C(8)	38.1 (3)	Mn-Fe-C(9)	156.7 (3)
C(1)-Fe-C(9)	96.8 (4)	C(2)-Fe-C(9)	120.7 (4)
C(7)-Fe-C(9)	64.7 (3)	C(8)-Fe-C(9)	38.9 (3)
Mn-Fe-C(10)	143.7 (3)	C(1)-Fe-C(10)	129.0 (4)
C(2)-Fe-C(10)	94.4 (3)	C(7)-Fe-C(10)	65.4 (3)
C(8)-Fe-C(10)	64.9 (4)	C(9)-Fe-C(10)	38.3 (3)
Mn-Fe-C(11)	106.7 (2)	C(1)-Fe-C(11)	158.9 (3)
C(2)-Fe-C(11)	103.9 (3)	C(7)-Fe-C(11)	38.5 (3)
C(8)-Fe-C(11)	63.9 (3)	C(9)-Fe-C(11)	64.1 (4)
C(10)-Fe-C(11)	39.0 (3)	C(12)-N(1)-C(13)	175.2 (5)
Fe-C(1)-O(1)	175.4 (7)	Fe-C(2)-O(2)	175.1 (6)
Mn-C(3)-O(3)	176.4 (6)	Mn-C(4)-O(4)	177.5 (6)
Mn-C(5)-O(5)	174.9 (6)	Mn-C(6)-O(6)	177.8 (5)
Fe-C(7)-C(8)	68.7 (4)	Fe-C(7)-C(11)	68.9 (4)
C(8)-C(7)-C(11)	105.5 (8)	Fe-C(8)-C(7)	73.2 (4)
Fe-C(8)-C(9)	70.0 (5)	C(7)-C(8)-C(9)	109.3 (8)
Fe-C(9)-C(8)	71.0 (4)	Fe-C(9)-C(10)	71.4 (5)
C(8)-C(9)-C(10)	109.0 (8)	Fe-C(10)-C(9)	70.3 (5)
Fe-C(10)-C(11)	70.9 (4)	C(9)-C(10)-C(11)	106.6 (8)
Fe-C(11)-C(7)	72.6 (4)	Fe-C(11)-C(10)	70.2 (5)
C(7)-C(11)-C(10)	109.7 (7)	Mn-C(12)-N(1)	177.1 (5)
N(1)-C(13)-C(14)	109.4 (1)	N(1)-C(13)-C(15)	109.3 (1)
C(14)-C(13)-C(15)	109.6 (1)	N(1)-C(13)-C(16)	109.3 (1)
C(14)-C(13)-C(16)	109.6 (1)	C(15)-C(13)-C(16)	109.6 (1)
N(1)-C(13)-C(14')	109.3 (1)	C(14)-C(13)-C(14')	56.6 (5)
C(15)-C(13)-C(14')	56.1 (5)	C(16)-C(13)-C(14')	141.4 (1)
N(1)-C(13)-C(15')	109.3 (1)	C(14)-C(13)-C(15')	56.0 (5)
C(15)-C(13)-C(15')	141.4 (1)	C(16)-C(13)-C(15')	56.7 (5)
C(14)-C(13)-C(15')	109.6 (1)	N(1)-C(13)-C(16')	109.4 (1)
C(14)-C(13)-C(16')	141.3 (1)	C(15)-C(13)-C(16')	56.5 (5)
C(16)-C(13)-C(16')	56.0 (5)	C(14')-C(13)-C(16')	109.6 (1)
C(15)-C(13)-C(16')	109.6 (1)	C(13)-C(14)-C(14')	61.7 (2)
C(13)-C(14)-C(15')	62.0 (2)	C(14')-C(14)-C(15')	120.1 (1)
C(13)-C(14)-C(16')	62.0 (2)	C(13)-C(15)-C(16')	61.7 (2)
C(14)-C(15)-C(16')	120.0 (1)	C(13)-C(16)-C(15')	61.7 (2)
C(13)-C(16)-C(16')	62.0 (2)	C(15)-C(16)-C(16')	119.9 (1)
C(13)-C(14)-C(14')	61.7 (2)	C(13)-C(14)-C(15)	61.9 (2)
C(14)-C(14)-C(15)	119.9 (1)	C(13)-C(15)-C(14)	62.0 (2)
C(13)-C(15)-C(16)	61.7 (2)	C(14)-C(15)-C(16)	120.0 (1)
C(13)-C(16)-C(15)	61.7 (2)	C(13)-C(16)-C(16)	62.0 (2)
C(15)-C(16)-C(16)	120.1 (1)		

highest peaks produced by the disorder. All calculations were performed on a Cyber-750 computer using the SHELX-76<sup>23</sup> system

**Table VI. Selected Torsion Angles for 3 and 4**

	torsion angle/deg	
	3 (M = Mn)	4 (M = Re)
C(3)-M-Fe-C(1)	61.2	35.0
C(3)-M-Fe-C(2)	155.1	127.1
C(4)-M-Fe-C(1)	156.3	124.9
C(4)-M-Fe-C(2)	109.8	143.0
C(5)-M-Fe-C(1)	32.0	54.9
C(5)-M-Fe-C(2)	61.9	37.2
C(12)-M-Fe-C(1)	119.7	145.2
C(12)-M-Fe-C(2)	25.8	53.1

**Table VII. Fractional Coordinates ( $\times 10^4$ ;  $\times 10^5$  for Re) and Equivalent Isotropic Temperature Factors ( $\text{Å}^2$ ,  $\times 10^3$ ;  $\times 10^4$  for Re) for Non-Hydrogen Atoms of 4**

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
Re	38098 (3)	8170 (3)	11881 (2)	353 (1)
Fe	3253 (1)	3356 (1)	1298 (1)	40 (1)
O(1)	1626 (8)	2639 (9)	2298 (6)	79 (6)
O(2)	5356 (8)	3335 (8)	2877 (6)	75 (5)
O(3)	1100 (7)	188 (9)	1064 (7)	81 (6)
O(4)	3011 (7)	1129 (7)	-879 (4)	59 (4)
O(5)	4558 (8)	654 (8)	3263 (5)	71 (5)
O(6)	4417 (7)	-1842 (6)	972 (5)	59 (4)
N	6554 (6)	1757 (7)	1354 (5)	43 (3)
C(1)	2270 (9)	2888 (9)	1891 (7)	52 (5)
C(2)	4532 (9)	3302 (9)	2253 (7)	52 (5)
C(3)	2100 (9)	439 (9)	1111 (7)	53 (5)
C(4)	3326 (8)	1044 (8)	-133 (6)	42 (4)
C(5)	4261 (9)	715 (8)	2516 (6)	48 (5)
C(6)	4209 (8)	-856 (8)	1059 (6)	45 (4)
C(7)	2350 (12)	3629 (10)	-70 (7)	60 (6)
C(8)	3651 (11)	3770 (9)	88 (7)	56 (6)
C(9)	4053 (12)	4750 (10)	703 (8)	62 (7)
C(10)	2949 (16)	5193 (10)	930 (8)	65 (7)
C(11)	1922 (13)	4518 (11)	465 (8)	65 (7)
C(12)	5578 (7)	1419 (8)	1275 (5)	39 (4)
C(13)	7823 (8)	2211 (8)	1570 (6)	44 (4)
C(14)	7792 (12)	3581 (10)	1781 (9)	69 (7)
C(15)	8321 (10)	1967 (14)	772 (8)	73 (7)
C(16)	8555 (10)	1499 (11)	2385 (8)	67 (6)

of programs. The molecular geometries of 3 and 4 with the numbering of the atoms are shown in Figures 2 and 3. Atomic parameters, bond lengths and angles, and selected torsion angles are given in Tables IV-VI and VI-VIII for 3 and 4, respectively. Listings of anisotropic thermal parameters, hydrogen atom coordinates, and calculated structure factors are included in the supplementary material.

## Results and Discussion

The photolytic reaction between equimolar amounts of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}_2(\text{CO})_{10}]$  has been reported to give an equilibrium mixture containing 25% **1** and 75% starting materials. This was confirmed by our own attempts to synthesize **1** photochemically.<sup>24</sup> To increase the yield of **1**, the starting material substrate ratios (Fe/Mn) were varied from 0.5/1 to 2/1 but quantitative NMR analysis of the reaction solutions revealed little alteration in the yield of the mixed dimer **1** (23% and 26%, respectively). The photolytic reaction between  $[\text{Re}_2(\text{CO})_{10}]$  and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2$  was also attempted, and NMR analysis of the equilibrium reaction mixture indicated formation of 20% **2**. Since the photolytic route to **1** and **2** gave only moderate yields of products, this route was not used for general synthetic purposes. The metathetical literature syntheses of **1**<sup>19</sup> and **2**<sup>20</sup> were thus investigated. These methods, starting from  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2\text{I}]$  and  $\text{Na}[\text{M}(\text{CO})_5]$  (M = Mn, Re) readily gave the required

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Table VIII. Bond Lengths (Å) and Angles (deg) for Non-Hydrogen Atoms of 4

Bond Lengths			
Re-Fe	2.893 (1)	Re-C(3)	1.948 (10)
Re-C(4)	2.004 (9)	Re-C(5)	2.003 (9)
Re-C(6)	1.929 (9)	Re-C(12)	2.074 (8)
Fe-C(1)	1.727 (10)	Fe-C(2)	1.756 (10)
Fe-C(7)	2.115 (10)	Fe-C(8)	2.130 (10)
Fe-C(9)	2.137 (10)	Fe-C(10)	2.113 (10)
Fe-C(11)	2.116 (10)	O(1)-C(1)	1.136 (11)
O(2)-C(2)	1.140 (11)	O(3)-C(3)	1.146 (11)
O(4)-C(4)	1.126 (10)	O(5)-C(5)	1.126 (11)
O(6)-C(6)	1.131 (11)	N-C(12)	1.137 (10)
N-C(13)	1.464 (10)	C(7)-C(8)	1.43 (2)
C(7)-C(11)	1.47 (2)	C(8)-C(9)	1.43 (2)
C(9)-C(10)	1.48 (2)	C(10)-C(11)	1.39 (2)
C(13)-C(14)	1.554 (13)	C(13)-C(15)	1.542 (14)
C(13)-C(16)	1.525 (13)		
Bond Angles			
Fe-Re-C(3)	89.0 (3)	Fe-Re-C(4)	86.7 (2)
C(3)-Re-C(4)	89.9 (4)	Fe-Re-C(5)	89.2 (3)
C(3)-Re-C(5)	89.9 (4)	C(4)-Re-C(5)	175.9 (4)
Fe-Re-C(6)	176.9 (3)	C(3)-Re-C(6)	92.7 (4)
C(4)-Re-C(6)	90.7 (4)	C(5)-Re-C(6)	93.4 (4)
Fe-Re-C(12)	84.7 (2)	C(3)-Re-C(12)	173.4 (4)
C(4)-Re-C(12)	89.6 (3)	C(5)-Re-C(12)	90.2 (3)
C(6)-Re-C(12)	93.6 (3)	Re-Fe-C(1)	85.8 (3)
Re-Fe-C(2)	83.0 (3)	C(1)-Fe-C(2)	91.6 (5)
Re-Fe-C(7)	97.3 (3)	C(1)-Fe-C(7)	113.5 (4)
C(2)-Fe-C(7)	155.0 (5)	Re-Fe-C(8)	92.8 (3)
C(1)-Fe-C(8)	152.3 (5)	C(2)-Fe-C(8)	115.8 (5)
C(7)-Fe-C(8)	39.3 (4)	Re-Fe-C(9)	123.1 (4)
C(1)-Fe-C(9)	151.1 (5)	C(2)-Fe-C(9)	92.9 (5)
C(7)-Fe-C(9)	65.9 (5)	C(8)-Fe-C(9)	39.3 (4)
Re-Fe-C(10)	159.6 (3)	C(1)-Fe-C(10)	111.0 (5)
C(2)-Fe-C(10)	107.1 (5)	C(7)-Fe-C(10)	66.0 (5)
C(8)-Fe-C(10)	66.9 (4)	C(9)-Fe-C(10)	40.7 (5)
Re-Fe-C(11)	132.8 (4)	C(1)-Fe-C(11)	92.6 (5)
C(2)-Fe-C(11)	144.0 (5)	C(7)-Fe-C(11)	40.5 (4)
C(8)-Fe-C(11)	67.3 (4)	C(9)-Fe-C(11)	66.9 (5)
C(10)-Fe-C(11)	38.5 (5)	C(12)-N-C(13)	173.0 (8)
Fe-C(1)-O(1)	176.4 (10)	Fe-C(2)-O(2)	176.2 (10)
Re-C(3)-O(3)	178.4 (10)	Re-C(4)-O(4)	176.6 (8)
Re-C(5)-O(5)	177.5 (9)	Re-C(6)-O(6)	178.6 (8)
Fe-C(7)-C(8)	70.9 (6)	Fe-C(7)-C(11)	69.8 (6)
C(8)-C(7)-C(11)	108.9 (10)	Fe-C(8)-C(7)	69.8 (6)
Fe-C(8)-C(9)	70.6 (6)	C(7)-C(8)-C(9)	107.9 (10)
Fe-C(9)-C(8)	70.1 (6)	Fe-C(9)-C(10)	68.8 (6)
C(8)-C(9)-C(10)	106.8 (11)	Fe-C(10)-C(9)	70.5 (6)
Fe-C(10)-C(11)	70.9 (6)	C(9)-C(10)-C(11)	109.2 (10)
Fe-C(11)-C(7)	69.7 (6)	Fe-C(11)-C(10)	70.6 (6)
C(7)-C(11)-C(10)	107.2 (11)	Re-C(12)-N	177.6 (7)
N-C(13)-C(14)	107.6 (8)	N-C(13)-C(15)	108.6 (7)
C(14)-C(13)-C(15)	112.4 (10)	N-C(13)-C(16)	105.8 (8)
C(14)-C(13)-C(16)	111.3 (9)	C(15)-C(13)-C(16)	110.8 (9)

products **1** and **2**. The products were easily separated from starting materials by column chromatography and after recrystallization were obtained in  $50 \pm 5\%$  yield (1–2-g scale). The reaction between  $[\text{Re}(\text{CO})_5\text{Br}]$  and  $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$  was also attempted to determine if the yield of **2** could be improved. However, in the above reaction, **2** was only obtained in 25% yield together with high yields of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Re}_2(\text{CO})_{10}]$ . The product distribution in the reaction may be attributed to the attack of **2** by the strong nucleophile  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$  which would lead to product breakdown and formation of the homometallic dimers.

The reaction between **2** and 1 equiv of L (L = *t*-BuNC, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, P(OMe)<sub>3</sub>, PMPh<sub>2</sub>) at 85–95 °C (see Experimental Section) led to the high-yield formation of the new substituted dimers  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4\text{L}]$ . The reaction occurred more rapidly for the isocyanides than

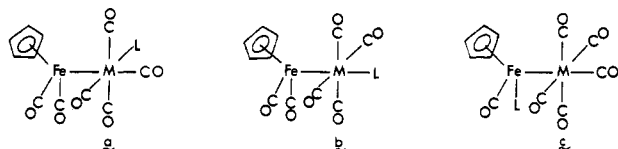


Figure 4. Possible monosubstituted derivatives obtained from the reaction of **1** or **2** and L (M = Mn, Re; L = RNC, P(OMe)<sub>3</sub>, PMePh<sub>2</sub>).

for P(OMe)<sub>3</sub> or PMePh<sub>2</sub>. Spectroscopic analysis, decomposition studies, and chemical studies (see below) were consistent with isolation of the Re-substituted product (Figure 4, part a or b). This was confirmed for L = *t*-BuNC by means of an X-ray crystal structure determination (see below).

Attempts to improve the reaction conditions or modify the reaction products, e.g. by obtaining the Fe-substituted derivative (Figure 4c), were undertaken. Addition of PdO as catalyst<sup>26</sup> to **2** and RNC (R = *t*-Bu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) at room temperature rapidly and cleanly gave the mono-Re-substituted derivatives (Figure 4a) in high yield. This result is entirely consistent with results obtained from the reaction between  $[\text{Re}(\text{CO})_5\text{Br}]$ <sup>27</sup> or  $[\text{Re}_2(\text{CO})_{10}]$ <sup>14</sup> and RNC (catalyzed by PdO under similar reaction conditions) and the reaction between  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ <sup>17</sup> and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}]$ <sup>26</sup> and RNC (not catalyzed by PdO under these conditions).

Addition of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  as catalyst<sup>17</sup> to the above reactions (25–80 °C) did not give an increase in reaction rate relative to the thermal noncatalyzed reactions, and the final products isolated were the Re-substituted derivatives. It had been anticipated that  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  would have induced reactivity at the Fe atom in **2**, had the reaction been catalyzed.

Me<sub>3</sub>NO has been widely used as a reagent in CO substitution reactions.<sup>28</sup> Further, it has been reported that the thermal and the Me<sub>3</sub>NO-assisted CO substitution reaction of  $[\text{H}_4\text{Rh}_4(\text{CO})_{12}]$  with diphos gives two different isomers of  $[\text{H}_4\text{Rh}_4(\text{CO})_{10}(\text{diphos})]$ .<sup>29</sup> Addition of Me<sub>3</sub>NO to **2** in CH<sub>3</sub>CN rapidly resulted in the disappearance of the starting material as determined by IR spectroscopy, and the new absorptions observed in the IR spectrum (see Experimental Section) suggested the presence of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  would have induced reactivity at the Fe atom in **2**, had the reaction been catalyzed.

Me<sub>3</sub>NO has been widely used as a reagent in CO substitution reactions.<sup>28</sup> Further, it has been reported that the thermal and the Me<sub>3</sub>NO-assisted CO substitution reaction of  $[\text{H}_4\text{Rh}_4(\text{CO})_{12}]$  with diphos gives two different isomers of  $[\text{H}_4\text{Rh}_4(\text{CO})_{10}(\text{diphos})]$ .<sup>29</sup> Addition of Me<sub>3</sub>NO to **2** in CH<sub>3</sub>CN rapidly resulted in the disappearance of the starting material as determined by IR spectroscopy, and the new absorptions observed in the IR spectrum (see Experimental Section) suggested the presence of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  would have induced reactivity at the Fe atom in **2**, had the reaction been catalyzed.

Our unsuccessful attempts to obtain the Fe-substituted derivative (Figure 4c) by a substitution reaction prompted us to attempt the synthesis of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNR})\text{Re}(\text{CO})_5]$  by alternative routes. The strategy was to react monometallic precursors containing a preformed Fe–RNC bond in metathetical metal–metal bond-forming reactions. Reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)\text{I}]$ <sup>17</sup> with  $\text{Na}[\text{Re}(\text{CO})_5]$  gave only  $[\text{Re}_2(\text{CO})_{10}]$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)]$ ,<sup>31</sup> presumably via a redox process.<sup>32</sup> Reaction of  $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)]$  with  $[\text{Re}(\text{CO})_5\text{Br}]$  resulted in a complex mixture of products characterized by

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NMR and IR spectroscopy as  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)]_2$ ,<sup>31</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}_2(\text{CO})_3(\text{CNBu-}t)]$ ,<sup>31</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{CNBu-}t)]$ ,  $[\text{Re}_2(\text{CO})_{10}]$ ,  $[\text{Re}_2(\text{CO})_9(\text{CNBu-}t)]$ ,<sup>14</sup> and  $[\text{Re}_2(\text{CO})_8(\text{CNBu-}t)_2]$ .<sup>14</sup> Also, reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)(\text{THF})][\text{BF}_4]$  (prepared from  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)\text{I}]$ <sup>17</sup> and  $\text{AgBF}_4$  in THF) with  $\text{Na}[\text{Re}(\text{CO})_5]$  at  $-20$  or  $25$  °C gave the Re-substituted derivative 4 as the main reaction product (50% yield as detected by NMR spectroscopy after benzene extraction from the crude product). Our inability to synthesize the Fe-substituted isocyanide derivative as well as the observation of Re-containing isocyanide products in the metathetical reactions implies that there is a facile migration pathway for transference of the RNC ligand from Fe to Re. Although all our above attempts are consistent with CO lability on the Re atom and not the Fe atom, the possibility of initial displacement of CO from Fe followed by transference of unsaturation to the Re atom cannot be completely excluded<sup>8</sup> (see below).

The direct reaction between  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5]$  (1) and L (L = *t*-BuNC, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, P(OMe)<sub>3</sub>, PMePh<sub>2</sub>) gave different reaction products to those obtained from the reactions of 2 with L. In these reactions iron-substituted salt products were formed in high yield (Table II) together with minor amounts of non-salt products. This is exemplified by the reaction of *t*-BuNC with 1. The addition of small amounts (0–1 molar equiv) of *t*-BuNC to 1 in THF at room temperature was monitored by IR spectroscopy, and the spectra indicated that portion of the starting materials was consumed and a salt product was formed as the major product ( $[\text{Mn}(\text{CO})_5]^-$  could readily be detected). Addition of 1 equiv of *t*-BuNC only resulted in consumption of half of the starting material; 2 equiv of *t*-BuNC were required to complete the reaction. Workup of the product, which included addition of  $\text{PF}_6^-$  to the reaction mixture, resulted in the isolation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)_2][\text{PF}_6]$  (70% yield) as characterized by IR and NMR spectroscopy. Similar results were obtained for the other ligands (see Table II).

Numerous attempts were made to increase the low yield (<5%) of the non-salt products, e.g.  $[(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_6(\text{CNBu-}t)]$ , formed in the reaction. However, slow dropwise addition of *t*-BuNC to 1, variation of the reaction temperature ( $-30$  to  $+40$  °C), and reaction solvent (benzene,  $\text{CHCl}_3$ ) did not increase the non-salt product yields significantly. Addition of PdO to solutions of 1 and L (L = P(OMe)<sub>3</sub>, PMePh<sub>2</sub>, *t*-BuNC;  $-30$  to  $+40$  °C) also did not affect the reaction, and again only the iron-substituted salt products were formed in significant amounts.

Addition of Me<sub>3</sub>NO to 1 in CH<sub>3</sub>CN resulted in changes in the solution IR spectrum, consistent with the formation of a  $[(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_6(\text{NCCH}_3)]$  complex. The NMR spectrum recorded in C<sub>6</sub>D<sub>6</sub> on this new complex ( $\delta$  4.36 (C<sub>5</sub>H<sub>5</sub>) and  $\delta$  0.26 (CH<sub>3</sub>CN); ratio ca. 5:3) further confirmed this proposal. Addition of *t*-BuNC or 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC to this reaction solution resulted in rapid formation of a new complex characterized by elemental analyses, IR and NMR spectroscopy, and decomposition studies (see below) as the Mn-substituted complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{CNR})]$ . Free CH<sub>3</sub>CN was generated in a reaction carried out in C<sub>6</sub>D<sub>6</sub> upon addition of RNC. An X-ray crystal structure determination of the complex with RNC = *t*-BuNC confirmed that equatorial substitution on Mn had occurred (Figure 2). Significantly, addition of P(OMe)<sub>3</sub> or PMePh<sub>2</sub> to the acetonitrile intermediate led only to the formation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}(\text{CO})_4\text{L}]_2$ <sup>33</sup> (L

= P(OMe)<sub>3</sub>, PMePh<sub>2</sub>), and not the required substituted dimer products.

Alternative routes to the synthesis of the monosubstituted derivatives via metathetical reactions involving isocyanide-substituted monometallic precursors were also attempted. Thus (i) reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}]$  and  $\text{Na}[\text{Mn}(\text{CO})_4(\text{CNBu-}t)]$  gave only  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$ , presumably via a redox process,<sup>32</sup> (ii) reaction of  $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$  and  $[\text{Mn}(\text{CO})_4(\text{CNBu-}t)\text{Br}]$ <sup>27</sup> resulted in the synthesis of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{CNBu-}t)]$  (30% yield), (iii) reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)\text{I}]$  and  $\text{Na}[\text{Mn}(\text{CO})_5]$  gave a range of products identified by IR and NMR spectroscopy as  $[\text{Mn}_2(\text{CO})_{10}]$ ,  $[\text{Mn}_2(\text{CO})_9(\text{CNBu-}t)]$ ,<sup>16</sup>  $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$ ,<sup>16</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_3(\text{CNBu-}t)]$ ,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5]$ , and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{CNBu-}t)]$ , and (iv) the reaction between  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)(\text{THF})][\text{BF}_4]$  and  $\text{Na}[\text{Mn}(\text{CO})_5]$  indicated formation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{CNBu-}t)]$ ,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)]_2$ , and  $[\text{Mn}_2(\text{CO})_{10}]$  as the main products and minor amounts of 1,  $[\text{Mn}_2(\text{CO})_8(\text{CNBu-}t)_2]$ , and  $[\text{Mn}_2(\text{CO})_9(\text{CNBu-}t)]$ . No Fe-substituted heterobimetallic dimer was observed in any of the above reactions, and it is apparent that, as with 2, isocyanide transfer from Fe to Mn is a facile process.

**Product Characterization.** Elemental analyses and NMR spectroscopy of the non-salt products from the reaction between 1 and 2 and L clearly indicated formation of a monosubstituted product but did not unambiguously establish the site of L in the product. Indeed, from the large downfield shift of the  $\eta^5\text{-C}_5\text{H}_5$  resonance, the NMR data suggested that substitution had occurred on the iron atom. IR spectra were complex. Mass spectral results for the isocyanide derivatives of 1 indicated fragments consistent with substitution at either Fe or Mn. For R = *t*-Bu, fragments at  $m/z$  232 (100% intensity) and  $m/z$  204 (20%) are observed. Possible assignments for the  $m/z$  232 fragments are  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-}t)]^+$  or  $[(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_2]^+$  and for  $m/z$  204 are  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CNBu-}t)]^+$  or  $[(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})]^+$ . Further, for R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>,  $m/z$  values at 298 (34% intensity) and 252 (27%) are observed which may be assigned to the  $[\text{Mn}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)]^+$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)]^+$  fragments, respectively. Mass spectral results obtained from the isocyanide derivative of 2 also suggested that substitution had occurred at either the Re or Fe atoms. Complete mass spectral fragmentation patterns are given in the supplementary material.

Photochemical studies in which reactions were monitored by NMR spectroscopy conclusively indicated that substitution of CO on 1 or 2 occurred at Mn or Re and not Fe. These studies performed on  $[(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_6\text{L}]$  (L = *t*-BuNC, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{FeRe}(\text{CO})_6\text{L}]$  (L = *t*-BuNC, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC, P(OMe)<sub>3</sub>, PMePh<sub>2</sub>) indicated smooth conversion of starting materials to  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{M}_2(\text{CO})_8\text{L}_2]$  (M = Mn, Re). The products were characterized by IR and NMR spectroscopy; in some instances products were isolated and separated by TLC prior to characterization. For M = Re or Mn and L = RNC the 1,2-diequatorial isomer was formed;<sup>14,16</sup> for M = Re and L = P(OMe)<sub>3</sub> and PMePh<sub>2</sub> the 1,2-diaxial isomer was obtained.<sup>34</sup> The thermal decomposition reaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_6\text{L}]$  (L = RNC),

(34) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Chem. Soc., Dalton Trans.* 1985, 2277.

(35) For other examples: Sbrignadello, G.; Bor, G.; Maresca, L. *J. Organomet. Chem.* 1972, 46, 345. Thornhill, G. J.; Manning, A. R. *Inorg. Chim. Acta* 1979, 33, 45.

also monitored by NMR spectroscopy, readily yielded  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and the diequatorial isomers of  $[\text{Mn}_2(\text{CO})_8(\text{CNR})_2]$  as the only reaction products (80 °C,  $\text{C}_6\text{D}_6$ ). A minor thermal decomposition reaction was observed for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4\text{L}]$  ( $\text{L} = t\text{-BuNC}$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{PMePh}_2$ ) (80 °C,  $\text{C}_6\text{D}_6$ , 90 min). These decomposition studies are consistent with substitution of the ligand at Mn or Re and not the Fe center. Finally, X-ray crystal structure determinations on  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{M}(\text{CO})_4(\text{CNBu-}t)]$  ( $\text{M} = \text{Mn, Re}$ ) confirmed that substitution had occurred at Mn and Re and at the expected equatorial site.

**Mechanistic Studies.** Studies on the substitution reactions of **2** suggest that the reactions occur via replacement of the CO ligand on the dimer molecule and do not involve the substitution of monomeric radical species: (i) Thermal studies have indicated that M–M bond cleavage only occurs at reasonable rates when  $T > 90$  °C; the substitution reactions occur at lower temperatures. (ii) No homonuclear dimer products are detected in the substitution reactions.

Reaction of **2** with L (via the thermal, PdO-catalyzed,  $\text{Me}_3\text{NO}$ -assisted reaction) yields in every instance the Re-substituted product. This could arise via one of two possibilities: (i) displacement of CO from the Re atom or (ii) displacement of CO from Fe followed by transfer of a CO group from Re to Fe and eventually substitution at Re (Sonnenberger–Atwood mechanism).<sup>8</sup> Our inability to prepare the iron-substituted isocyanide complex does not allow us to conclusively differentiate between the two possibilities, although qualitative rate data suggests a ligand-dependent reaction that would preclude the second mechanism. Also, studies on related  $[\text{Re}(\text{CO})_5\text{X}]$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}]$  species suggest that substitution occurs initially at the Re atom (see above). The possibility that cis-labilizing effects<sup>36</sup> are dominant must be considered. For instance the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$  unit may enhance labilization of a CO group on  $\text{Re}(\text{CO})_5$  (relative to the reverse cis-labilization effect), but more detailed studies will be required to resolve this issue.

The reaction between **1** and L ( $\text{L} = \text{RNC}$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{PMePh}_2$ ) proved to be more complex and yielded in every instance salt products. This suggests an alternative mechanism must be operative in these reactions. Again, it seems unlikely that the substitution reaction occurs via breakdown of the dimer into monometallic radicals as no homonuclear dimer products were detected and the thermal metal–metal bond cleavage reaction occurs at a higher temperature than the substitution reaction.

To determine whether the substitution reaction occurs via displacement of  $[\text{Mn}(\text{CO})_5]^-$  from L acting as a nucleophile to yield  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{L}]^+$ , the salts  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{L}][\text{BF}_4]$  ( $\text{L} = t\text{-BuNC}$ , 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$ ) were independently synthesized by known procedures. The reaction between the above salts and an equivalent of the corresponding isocyanide was attempted. No reaction, as detected by IR spectroscopy, occurred, even in the presence of added **1** as possible catalyst. (The counterion in our model reaction is not the same as in the reaction mixture (viz.  $\text{BF}_4^-$  vs.  $[\text{Mn}(\text{CO})_5]^-$ ), and it is possible that this could result in a change in the rate of the reaction.) These results preclude this pathway as a major pathway leading to the observed products. The data are not however inconsistent with an electron-transfer mechanism as

has been proposed for the substitution reaction of many homonuclear dimer carbonyl complexes.<sup>38</sup>

In the  $\text{Me}_3\text{NO}$  reaction, **1** produces  $[(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_6(\text{NCCH}_3)]$ . As with the reaction of **2** with ligands L, it is not certain whether a CO molecule on Fe or Mn was displaced from **1**. However, from the known reactions of the monometallic dimers, substitution at Mn may be expected (see above). Further substitution of  $\text{CH}_3\text{CN}$  by RNC leads to the Mn-substituted dimer. The crystal structure determination of **3** reveals a remarkable displacement of the  $t\text{-BuNC}$  group away from the Fe atom (i.e.  $\text{Fe–Mn–CNR}$  angle = 97°) and would suggest that the molecule is sterically crowded. Consistent with this result is the observation that addition of  $\text{P}(\text{OMe})_3$  or  $\text{PMePh}_2$  to  $[(\eta^5\text{-C}_5\text{H}_5)\text{FeMn}(\text{CO})_6(\text{NCCH}_3)]$  leads to  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and  $[\text{Mn}_2(\text{CO})_8\text{L}_2]$  and not the axially substituted mixed-metal dimer. The larger cone angle of the group 15 donor ligands could be responsible for the breakdown of the mixed dimer. This steric crowding may also be responsible for the salt-forming reactions described above.

A consideration of the final (thermodynamic) products for the thermal reaction between **2** and L indicates  $\text{Re}(\text{CO})_5 > (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$  (monosubstitution occurs at Re in preference to Fe). The literature also reveals other instances of preferential substitution reactions of mixed-metal dimers, viz. at Re in  $[\text{MnRe}(\text{CO})_{10}]$ ,<sup>8,14</sup> at Co in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Co}(\text{CO})_4]$ <sup>37a</sup> and at Co in  $[\text{Mn}(\text{CO})_5\text{Co}(\text{CO})_4]$ .<sup>37b</sup> It thus becomes possible to produce a limited but consistent series for establishing the products from the direct thermal reaction between metal carbonyl fragments in heteronuclear dimer complexes and L:  $\text{Re}(\text{CO})_5$ ,  $\text{Co}(\text{CO})_4 > (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ ,  $\text{Mn}(\text{CO})_5$ .

Our data have indicated that it is possible to modify the position of attack on the metal dimers and thus invert the reaction sequence listed. Further studies will be needed to elaborate on the scope of this approach. Finally, of significance was the observation that no iron-substituted derivatives of **1** or **2** were synthesized and that transfer of RNC from Fe to Re seems a facile process. Factors responsible for this effect (e.g. steric crowding) still need to be ascertained.

**X-ray Structure Determinations of 3 and 4.** The X-ray structure determinations of both **3** and **4** revealed that there were no bridging or semibridging CO<sup>39</sup> groups (closest MCO  $\cdots$ M' interaction = 2.95 Å) and that the two halves of the molecule were only held together by a single metal–metal bond. The ligand arrangement around the Mn, Re, and Fe atoms is close to octahedral ( $\text{C}_5\text{H}_5$  ring occupying three coordination sites<sup>40</sup>), and the Newman projections viewing **3** and **4** down the metal–metal bond indicates the nearly staggered arrangement of the  $t\text{-BuNC}$  and CO groups on the two metal halves (Figure 5 and Table VI). In both structures the expected<sup>34</sup> equatorial substitution of CO by  $t\text{-BuNC}$  was observed on the non-Fe atoms.

The Mn–Fe bond length in **3** (2.841 (1) Å) is very close to that observed in the unsubstituted dimer **1** (2.843 (4) Å).<sup>41</sup> In previous studies involving related comparisons between unsubstituted and isocyanide-substituted metal dimers, we have also noted minor changes in the metal–metal bond length on dimer substitution.<sup>34</sup> This measurement seems to be very insensitive to the steric/electronic changes that have occurred on substitution but are

(38) See, for example: Absi-Halabi, M.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *J. Am. Chem. Soc.* 1980, 102, 6248.

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(37) (a) Davey, G.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* 1974, 698. (b) Sbrignadello, G.; Bor, G.; Maresca, L. *J. Organomet. Chem.* 1972, 46, 345.



**Table IX. Bond Length Data for Some Unsubstituted and Isocyanide Substituted Dimers**

complex	bond length/Å	ref
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ cis	2.531 (2), 2.534 (2)	c, d
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ trans	2.5389 (3), 2.5390 (6) <sup>a</sup>	e
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3(\text{CNBu-t})]^b$	2.524 (2)	f
$[\text{Mn}_2(\text{CO})_{10}]$	2.904 (1)	g
$[\text{Re}_2(\text{CO})_{10}]$	3.041 (1)	g
$[\text{Re}_2(\text{CO})_9(\text{CNBu-t})]$	3.048 (1)	h
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5]$	2.843 (4)	i
3 (obsd)	2.841 (1)	this work
3 (calcd) <sup>j</sup>	2.720	
4 (obsd)	2.893 (1)	this work
4 (calcd) <sup>j</sup>	2.789	

<sup>a</sup>Neutron diffraction study. <sup>b</sup>Terminal isocyanide ligand.

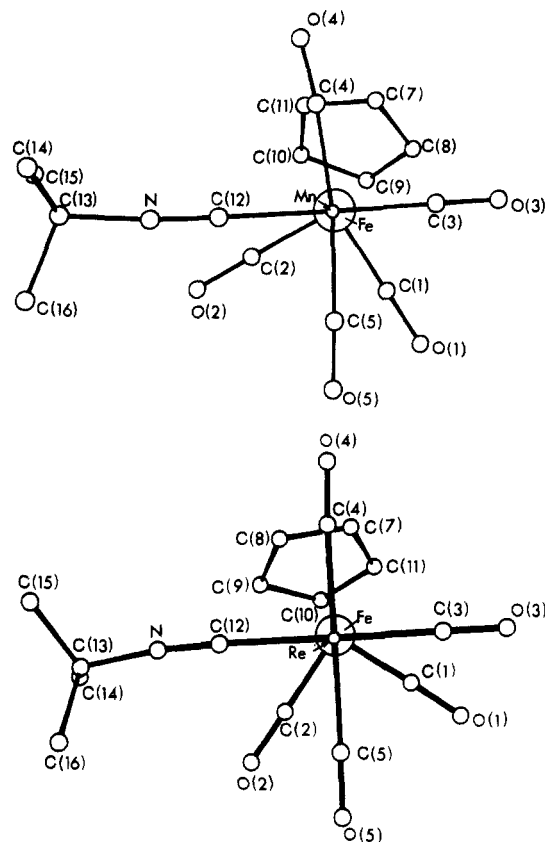
<sup>c</sup>Bryan, R. F.; Greene, P. T.; Newlands, M. J.; Field, D. S. *J. Chem. Soc. A* **1970**, 3068. <sup>d</sup>Bryan, R. F.; Greene, P. T. *J. Chem. Soc. A* **1970**, 3064. <sup>e</sup>Mitschler, A.; Rees, B.; Lehmann, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 3390. <sup>f</sup>Adams, R. D.; Cotton, F. A.; Troup, M. A. *Inorg. Chem.* **1974**, *13*, 257. <sup>g</sup>Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609. <sup>h</sup>Reference 34. <sup>i</sup>Reference 41. <sup>j</sup>Calculated from  $d_{m-m'} = 1/2(d_{m-m} + d_{m-m'})$ .

readily detected by spectroscopic techniques.<sup>42</sup> A comparison of the bond length with other Mn–Fe bonds in a wide range of dimer and trimetallic complexes suggests that the value, although long, is not unusual.<sup>43</sup> (Mn–Fe bond lengths studied vary between 2.539 (1)<sup>44</sup> and 2.843 (4)<sup>41</sup> Å.) The above data (unbridged metal atoms, long Mn–Fe bond) are consistent with the chemical properties associated with the molecule; in particular the facile cleavage of the M–M bond under chemical and thermal conditions.

The Re–Fe bond length (2.893 (1) Å), to our knowledge the first reported Re–Fe bond length, is only slightly longer than the Mn–Fe bond length (0.05 Å). However, this minor increase has important consequences on the chemical properties of 4 and on the ligand–ligand interactions between the two halves of the molecules (see below).

A comparison of the bond length data for pertinent substituted and unsubstituted monometallic dimers is given in Table IX. With use of these data, it is found that the calculated bond lengths for 3 and 4 are all shorter than those measured (Table IX). This could in part be due to the lack of bridging carbonyl groups in the heteronuclear dimers. It is to be noted however that the difference between the observed and calculated M–M bond lengths increases for the Mn–Fe bond relative to the Re–Fe bond (0.123 Å for 1 and 0.103 Å for 2).

The most significant structural features relate to the M–M–CNR and M–M–CO (trans to CNR) bond angles. For structure 3 the Fe–Mn–C(3) angle is 74.8 (2)° and Fe–Mn–C(12) is 97.1 (2)° (only slight bending in equatorial ligands toward the metal–metal bond is expected<sup>45</sup>). This data would imply a repulsion between the CNR group and groups on the Fe atom. The Newman projection (Figure 5) indicates that this could be a consequence of an interaction with the carbonyl group C(2)–O(2) attached to Fe. The equivalent bond angles in 4 show a reverse situation which is also less significant than that observed in 3. In this structure the Fe–Re–C(3) angle is normal, 89.0 (3)° but the Fe–Re–C(12) now is acute, 84.7 (2)°. The Newman



**Figure 5.** Newman projection of 3 and 4 viewed down the M–M bond.

projection indicates that the RNC group does not interact significantly with carbonyl C(2)–O(2). It is also to be noted that bond angle data reported for 1 indicate that two Fe–Mn–CO angles are acute (76–83°) and these two CO groups bend in *toward* the cyclopentadienyl ligand.<sup>41</sup> The data thus suggest that minor twists in the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$  unit results in significant steric effects on the equatorial groups bonded to Mn or Fe. The final geometry adopted must result from the best steric arrangement of the ligands. Importantly, even though steric effects are suggested in 1 and 3, the metal–metal bond length does not reflect these steric interactions.

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**Registry No.** 1, 12088-73-2; 2, 12088-76-5; 3, 108008-98-6; 4, 108008-99-7;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ , 12078-28-3;  $\text{Na}[\text{Mn}(\text{CO})_5]$ , 13859-41-1;  $\text{Na}[\text{Re}(\text{CO})_5]$ , 33634-75-2;  $[\text{Mn}_2(\text{CO})_{10}]$ , 10170-69-1;  $[\text{Re}_2(\text{CO})_{10}]$ , 14285-68-8;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNBu-t})_2][\text{PF}_6]$ , 108009-00-3;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)_3][\text{PF}_6]$ , 108008-88-4;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PMePh}_2)_2][\text{PF}_6]$ , 108009-01-4;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{P}(\text{OMe})_3)_2][\text{PF}_6]$ , 72167-18-1;  $[\text{Mn}(\text{CO})_4(\text{P}(\text{OMe})_3)_2]$ , 15529-61-0;  $[\text{Mn}(\text{CO})_4(\text{PMePh}_2)_2]$ , 63393-52-2;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ , 12154-95-9;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Mn}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$ , 108008-89-5;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{W})_2(\text{CNBu-t})][\text{BF}_4]$ , 108008-91-9;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{W})_2(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)][\text{BF}_4]$ , 108008-93-1;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{W})_2(\text{CH}_2\text{Cl}_2)][\text{BF}_4]$ , 108008-95-3;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]$ , 108008-96-4;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{PMePh}_2)]$ , 108034-77-1;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{P}(\text{OMe})_3)]$ , 108008-97-5;  $\text{PdO}$ , 11113-77-2.

**Supplementary Material Available:** Tables of anisotropic temperature factors, fractional coordinates and isotropic temperature factors of the H atoms, and bond lengths involving H for 3 and 4 and mass spectral data (12 pages); listings of observed and calculated structure factors for 3 and 4 (35 pages). Ordering information is given on any current masthead page.

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